



# Synthesis and characterization of novel fluorene-based green copolymers and their potential application in organic light-emitting diodes

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## ABSTRACT

Fluorene-benzothiadiazole (PFBT), commercially known as F8BT, and fluorene-thiophene (PFT) copolymers were synthesized by the Suzuki-Miyaura coupling polycondensation technique in the presence of a phase transfer catalyst (Aliquat 336). These novel copolymers showed higher molar masses, lower dispersivity, and thermal stability above 400 °C when synthesized under the modified (M) action of Aliquat 336 (F8BT-M). Polymer Light-emitting diodes (PLEDs) were assembled with the novel synthesized copolymers as the emitter layer. For F8BT-M, a maximum luminance of 327 cd/m<sup>2</sup> was achieved, while a diode containing just the commercial F8BT resulted in only 210 cd/m<sup>2</sup>. As for the PFT copolymers, it was observed that for the Aliquat 336 sample synthesized in a 60h extended (E) (PFT-ME), the luminance of the PLED was much higher than that where the reaction time was 48 h (PFT-M), with a luminance of 168 cd/m<sup>2</sup> and 54 cd/m<sup>2</sup>, respectively. Without Aliquat 336, the PFT copolymer did not show an electroluminescent signal. The improved electroluminescence in the copolymers with Aliquat 336 was attributed to the improved synthesis conditions, i.e., reaction time and catalytic system employed. The results suggest that copolymers with luminescent and morphological properties, more suitable for light-emitting devices, might be obtained with simple modifications during synthetic polycondensation reactions.

## 1. Introduction

The synthesis of light-emitting alternating copolymers has attracted significant attention over the years since such materials have low bandgap and broad and intense absorption in the visible and near-infrared regions, in addition to exhibiting a good fit of the *Lowest Unoccupied Molecular Orbital* (LUMO) position [1–4]. Such aspects arise from the delocalization of  $\pi$  electrons in the backbone of conjugated polymers that can induce strong stacking interactions, facilitating the efficient transport of charge carriers and, thus, increasing the electrical conductivity [5].

Among conjugated polymers, fluorene copolymers (PFs) have been extensively studied as one of the main classes of emitting materials used as an active layer in polymer light-emitting diodes (PLEDs) due to their good processability and high luminescence quantum yields [6–8]. Furthermore, PF can be easily functionalized at the 9 position with a long alkyl side chain to improve material solubility. In addition, its emission can be modified by adding different groups to the polymeric chain [8–10]. Thus, PF as a donor moiety in copolymers has aroused considerable research interest for application in PLEDs, revealing better thermal and oxidative stability, high photoluminescence (PL) and electroluminescence (EL), as well as long service life and tunable properties

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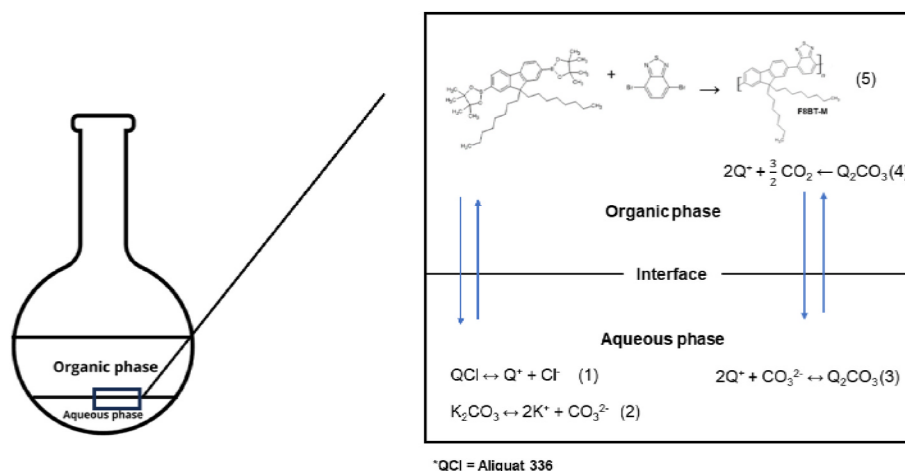


Fig. 1. Action of Aliquat 336 in polycondensation reactions such as F8BT polymerization.

to cover the entire visible range of wavelength [11–13].

To obtain adjustable EL properties, different groups can be inserted into the main polymer chain, such as benzothiadiazole, thiophene, and thieno-arenes [8,10–15]. Among the fluorene copolymers that have the highest photoluminescence quantum yield (PLQY), poly (9,9-dioctylfluorene-co-benzothiadiazole) (PFBT), commercially known as F8BT, stands out for high stability and good charge transport properties [16]. It delivers good performances when applied as an active layer in PLEDs, where it has demonstrated high hole mobility, providing devices with high efficiencies [17,18]. However, the electron localization on the benzothiadiazole (BT) unit may decrease electron mobility in F8BT, blocking electron injection at the interface of F8BT/cathode [14,19–22].

Even so, the F8BT conjugated polymer is an efficient emitter of green light, with a PL efficiency of 50–60 % in films. Furthermore, it exhibits a relatively high electron affinity, equivalent to 3.3 eV, and a large ionization potential of 5.9 eV [23]. Alternatively, introducing thiophene units in the fluorene chain promotes good stability in the neutral and doped states, which can propitiate the emission's displacement and decrease the formation of aggregates [24–28].

Among the characteristics that influence the electrical and optical performance of polymer materials, the weight molar mass ( $M_w$ ) is one of the essential parameters [29,30]. Their syntheses are mostly performed by the Suzuki-Miyaura coupling technique in an interfacial system under the action of a Pd catalyst [31,32]. Some studies report adding a phase transfer agent for greater interaction of the reactants in the reaction medium [33–39]. One widely reported phase transfer agent is the Starks' catalyst (tricapryl methylammonium chloride), known as Aliquat 336, a mixture of quaternary ammonium salts (ionic liquid), which scavenges anions such as  $\text{Cl}^-$  and  $\text{Br}^-$  [40,41]. Aliquat 336 is commonly used as a surfactant and phase transfer catalyst, as it has a strong chloride anion coordination effect [40,42]. Studies indicate that Aliquat 336 can provide a higher degree of polymerization and  $M_w$ , as well as reduce the dispersity in polymerizations by Suzuki-Miyaura coupling [43].

Polymerization by the Suzuki-Miyaura is a step-growth polycondensation characterized by cross-coupling two aryl subunits, one from an aryl diboronic acid and the other from an organodihalide, catalyzed by heterogeneous Pd compounds in two-phase, water and organic solvent. This system also comprises an organodiboronate complex, partitioning between the aqueous and organic phases [44]. Therefore, a phase transfer agent such as Aliquat-336 enables reactions between anions or molecules soluble in the aqueous phase and organic substrates soluble in the organic phase [45], acting as a surfactant. According to Said and Ben [46], the use of Aliquat-336 plays an important role in the reduction of Pd(II) as well as in the stabilization and solubilization of Pd (0).

In the literature, F8BT copolymers with number-average molar masses ( $M_n$ ) of 3.8, 6.7, 9.9 and 15 kDa were synthesized and characterized. All polymers exhibited fine-tuned energy levels with better ambipolar carrier mobility [47]. Wang et al. [48] reported an F8BT copolymer with a  $M_n$  of 23500 g/mol. While in the work of Santos et al. [33], such copolymer had an  $M_n$  of 9225 g/mol. A possible explanation for the difference is that the latter did not employ Aliquat 336 in the reaction medium and terminated the chain with phenylboronic acid and bromobenzene. Azevedo et al. [49] used an F8BT copolymer with  $M_n$  of 22000–24000 g/mol in a single-layer polymer light-emitting diode. Morais et al. [14] synthesized PFBT. Their reaction medium consisted of the monomers 9,9-dihexylfluorene-2,7-diboronic acid, 4,7-dibromobenzoyl-1,2,5-thiadiazole. Using a potassium carbonate solution, toluene as solvent, and the Pd phosphine catalyst ( $\text{Pd}(\text{PPh}_3)_4$ ), the reaction was carried out at 95 °C for 72 h, and the obtained copolymer presented  $M_n$  around 2630 g/mol and dispersity ( $\text{Đ}$ ) of 2.32.

Vamvounis et al. [50] reported that the average  $M_n$  for the fluorene-co-thiophene (PFT) copolymer was around 6254 g/mol with a  $\text{Đ}$  of 1.3 employing the Pd catalyst ( $\text{Pd}(\text{PPh}_3)_4$ ) and tetrahydrofuran (THF) as solvent. Pal et al. [13] reported  $M_n$  of 2904 g/mol and  $\text{Đ}$  of 1.68. Rodrigues et al. [51] synthesized the copolymer poly [(9,9-dioctylfluorene)-co-thiophene] (PDOF-co-Th) using the monomers 9,9-dioctylfluorene-2,7-diboronic acid and 2,5-dibromothiophene. The reaction medium consisted of a potassium carbonate solution, xylene as a solvent and a Pd catalyst, the reaction time was 72 h. The obtained copolymer presented  $M_n$  of 2009 g/mol and  $\text{Đ}$  of 5.29.

The present work aims to synthesize novel green emission organic materials based on F8BT and PFT copolymers in the presence of Aliquat 336 in order to evaluate how those innovative modifications in the synthetic procedure affect the properties of the materials, such as thermal stability,  $M_w$ , and absorbance and photoluminescence. To evaluate the electroluminescence properties, PLED devices were assembled with such copolymers as light emitting materials, employing the architecture, glass-ITO/PEDOT:PSS/PVK/green light emitting copolymer/Ca/Al [52, 53], and the characteristics achieved for the devices are discussed.

## 2. Experimental

### 2.1. Materials

For the synthesis of the F8BT copolymer, the monomers 2,2'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis (4,4,5,5-tetramethyl-1,3,2-dioxaborolane from Oxchem Corp, USA, and 4,7-dibromobenzo [c] [1,2,5]thiadiazole from Ossila, UK, were used. For the synthesis of the PFT copolymer, the monomers were 9,9-dioctylfluorene-2,7diboronic acid and 2,5-dibromo-3-hexylthiophene, purchased from Henan Alfachem

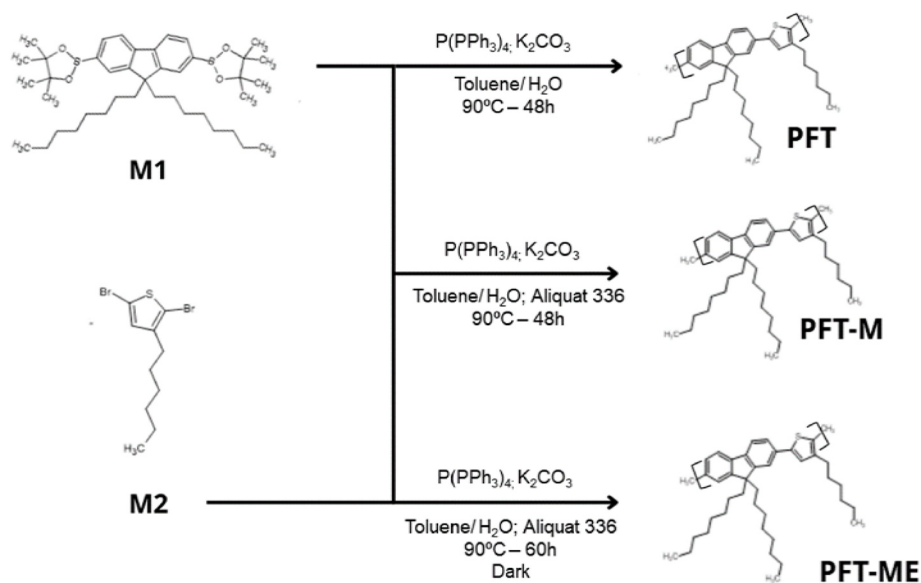


Fig. 2. Synthetic routes performed for fluorene-thiophene copolymers.

Co, China, and Okwood Chemical, USA, respectively. Pd catalyst ( $\text{Pd}(\text{PPh}_3)_4$ ) was purchased from Sigma Aldrich, Brazil, as well as the potassium carbonate and Ca. The Aliquat 336 was purchased from Oakwood Chemical, and the phenylboronic acid from OxChem. The solvent used in both syntheses, toluene, was supplied by ProQuimios, Brazil, and distilled under Na. The PLEDs based on the synthesized materials were assembled using Corning, USA, Eagle XG/1737 indium-doped tin oxide (ITO) conductive glasses with a resistance of 7–10  $\Omega/\text{sq}$  sheet and poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) Clevios P VP AI 4083, from H.C. Starck, USA. Poly(9-vinylcarbazole) (PVK,  $M_w \sim 1,100,000$ ) was purchased from Sigma Aldrich. Commercial F8BT ( $M_n < 25000$  g/mol,  $\text{D} < 3$ ), used as standard material for comparison, was acquired from Sigma Aldrich.

## 2.2. Methods

Fig. 1 presents the reactions that characterize the copolymerization of the monomers 2,2'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (M1) and 4,7-dibromobenzothiazole (M2) mediated by  $\text{K}_2\text{CO}_3$ /Aliquat 336 in Toluene/water biphasic systems. The dissociation reaction of tetrabutylammonium chloride (QCl- Aliquat 336) and  $\text{K}_2\text{CO}_3$ , resulting in the formation of  $\text{Q}_2\text{CO}_3$  in the aqueous phase with subsequent transfer to the organic phase, occurs throughout the reactions, as evidenced by Eqs. (1)–(4), displayed in Fig. 1. Eq. (5), the polycondensation reaction between the boronate and bromine groups of the monomers was demonstrated.

The synthesis of F8BT-M was carried out in a round bottom flask under a nitrogen atmosphere by adding 1 mmol of M1, 1 mmol of M2, and 34.7 mg of the catalyst  $\text{Pd}(\text{PPh}_3)_4$  in 12 mL of toluene. Then, 2 mL of potassium carbonate 2 M aqueous solution ( $\text{K}_2\text{CO}_3$  acting as the base) were added, and subsequently, 10 drops of Aliquat 336 were added. A condenser previously closed with a septum was attached to the flask. After 24 h, 0.121 g of phenylboronic acid was injected as a polymer chain terminal group, and the reaction was maintained under heating and stirring for another 48 h. The organic phase was extracted with chloroform at the end of this process, and the mixture was then filtered. Magnesium sulfate was added to the filtrate and left stirring for 1 h. After this time, the mixture was filtered again, and chloroform was removed by rotary evaporation. The polymer was precipitated in methanol, obtaining a bright yellow fibrous material. The precipitated material was filtered, dried, and purified by Soxhlet extraction in acetone, hexane, and chloroform. The F8BT-M was collected in chloroform and dried

in a Petri dish, forming a homogeneous shiny film. The nuclear magnetic resonance (NMR) signals corresponding to F8BT-M ( $\text{CDCl}_3$ ), are  $\delta = 8.10$  (d, 2H), 7.97 (m, 6H), 8.04 (s, 2H), 2.16 (s, 4H), 1.16 (m, 20H), 0.97 (s, 4H), 0.81 (m, 4H).

The three methodologies illustrated in Fig. 2 were used to develop fluorene-thiophene copolymers. The first was without using a phase transfer agent, with a reaction time of 48 h (PFT). The second with the phase transfer agent Aliquat 336, also for 48 h of reaction time (PFT-M). The third was carried out with Aliquat 336 agent and performed in the dark for 60 h of synthesis (PFT-ME).

For the synthesis of PFT: 5 mmol of M1 (9,9-dioctylfluorene-2,7-diboronic acid), 5 mmol of M2 (2,5-dibromo-3-hexylthiophene), and 0.020 g of  $\text{Pd}(\text{PPh}_3)_4$  were added to a round bottom flask. 12 mL of toluene and 8 mL of  $\text{K}_2\text{CO}_3$  solution (2 M) were added. The mixture was stirred vigorously at 85–90  $^\circ\text{C}$  for 48 h under  $\text{N}_2$ . After the reaction time, the polymer chain was terminated with phenylboronic acid and maintained for another 24 h. After introducing the chain terminal group, the reaction was cooled to room temperature (RT), the organic phase was extracted into chloroform, and a desiccant agent was added. The medium was filtered and poured into a mixture of methanol and water (10:1). A yellow fibrous solid was obtained. The solid was then filtered and washed with methanol, water, and methanol. The material was purified by washing with acetone in a Soxhlet apparatus for 24 h to remove oligomers and catalyst residues, then with hexane, and finally with chloroform, where the polymer was collected. It was then dried in a Petri dish at RT. The corresponding PFT  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) signals are  $\delta$  7.61 (dd,  $J = 70.6, 50.8$  Hz, 6H), 7.32 (s, 2H), 2.05 (m, 4H), 1.10 (m, 16H), 0.85 (d,  $J = 34.4$  Hz, 14H).

The same procedure as for PFT was employed for PFT-M synthesis, except for introducing 10 drops of Aliquat 336 to the reaction medium. The reaction was also conducted at 90  $^\circ\text{C}$  for 48 h. The terminal group phenylboronic acid was added under the same reaction conditions. Likewise, the material was subjected to Soxhlet extraction in acetone, hexane, and then chloroform for purification. The corresponding PFT-M  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) signals are  $\delta$  7.61 (dd,  $J = 70.6, 50.8$  Hz, 6H), 7.32 (s, 2H), 2.05 (m, 4H), 1.10 (m, 16H), 0.85 (d,  $J = 34.4$  Hz, 14H).

The conditions for the PFT-ME synthesis were the same as PFT-M, with the difference that the reaction was carried out in the dark for 60 h to investigate the influence of the reaction time on the  $M_w$  of the synthesized copolymer. This synthesis was performed in the dark because the possible photosensitivity of the boronate group in one of the monomers was noted. The methodology used to obtain PFT is described

by Chen et al. [48]. After closing the polymeric chain, the material was precipitated in methanol, filtered, and treated by Soxhlet extraction in acetone, hexane, ethyl acetate, and dichloromethane. The polymer was collected in the hexane fraction, and in the other solvents, there was no extraction. The corresponding PFT-ME  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) signals are  $\delta$  7.86–7.56 (m, 6H), 7.53–7.29 (s, 2H), 2.05 (m, 4H), 1.45–0.99 (m, 16H), 0.95–0.61 (m, 14H).

### 2.3. Characterization

Using gel permeation chromatography (Prominence® UFLC Shimadzu with Shim-pack GPC-803C column set,  $300 \times 8.0$  mm ( $M_w$ ):  $7 \times 10^4$  and Phenogel™ 5  $\mu\text{m}$  Linear (2),  $300 \times 7.8$  mm ( $M_w$ ):  $1 \times 10^7$ ), the  $M_w$  of the synthesized copolymers were measured. The emitting materials were dissolved in chloroform at a 2 mg/mL concentration and injected into the chromatograph using  $\text{CHCl}_3$  as an eluent. A calibration curve was based on monodispersed polystyrene standards. Thus, the weight average  $M_w$ ,  $M_n$  and  $\bar{D}$  were obtained.

To confirm the structure of the synthesized copolymers (F8BT-M, PFT, PFT-M, and PFT-ME),  $^1\text{H}$  NMR spectroscopy was performed in a Bruker® spectrometer at 400 and 500 MHz using  $\text{CDCl}_3$  as solvent. The structure was also investigated by Fourier transform infrared spectroscopy on an Infrared Spectrometer - Spectrum 100 - PerkinElmer in ATR mode in the wavelength range of  $580\text{--}4000$   $\text{cm}^{-1}$ .

Thermogravimetric analysis (TGA) was used to determine the thermal stability of the emitting materials. Samples in powder or film (10 mg) were analyzed in a TA Instruments Q500 equipment under a nitrogen atmosphere ( $\text{N}_2$  flow of 60.0 mL/min), from RT to  $700$   $^\circ\text{C}$ , at a heating rate of  $10$   $^\circ\text{C}/\text{min}$ . Through this analysis, the initial degradation temperature ( $T_{\text{onset}}$ ), the temperature of the maximum degradation rate ( $T_{\text{max}}$ ), identified as the peak in the derived thermogravimetry, as well as the residue obtained at the end of the analysis ( $700$   $^\circ\text{C}$ ) were determined.

X-ray diffraction analysis (XRD) was conducted in a Rigaku diffractometer (Miniflex model), with a potential difference of 30 kV and an electric current of 15 mA. The samples were deposited from solutions of 10 mg/mL in chloroform to form a film on a glass substrate and subjected to a scan in the range of  $2\theta$  from  $2^\circ$  to  $45^\circ$  at  $0.05^\circ/\text{min}$  and  $\text{CuK}\alpha = 1.5418$   $\text{\AA}$ .

The copolymer solutions were prepared to obtain the ultraviolet–visible (UV–Vis) absorption spectra, and the samples were diluted in chloroform (1 mg/mL). Measurements were performed using an Agilent Cary 60 UV–Vis spectrophotometer.

With the device ready, the roughness of the polymeric films deposited as an emitter layer (EML) was evaluated by atomic force microscopy (AFM) using a Nanosurf C3000 microscope operating in non-contact mode with a speed of  $5$   $\mu\text{m}/\text{s}$  and an area of  $20 \times 20$   $\mu\text{m}$ . The images generated by the equipment were processed using the Gwyddion software (64 bits).

To perform the cyclic voltammetry (CV) analysis, the copolymers were deposited (200  $\mu\text{L}$  of a 5 mg/mL solution) by spin-coating on ITO-glass substrates and subsequently heat treated at  $100$   $^\circ\text{C}$  for 10 min. Measurements were carried out in a Metrohm Autolab potentiostat with a three-electrode cell in a solution of tetrabutylammonium hexafluorophosphate ( $\text{TBAPF}_6$ ) in acetonitrile (0.1 M) bubbled with nitrogen, at a sweep rate of 20 mV/s, at RT. Ag/AgCl was used as the reference electrode, a Pt wire was used as the counter electrode, and the working electrode was the ITO-glass substrate coated with the copolymers. HOMO energy levels were obtained from the equation  $\text{HOMO} = -(\text{E}_{\text{oxonset}} + 4.8)$  eV. The LUMO levels of the polymers were obtained between the difference  $\text{E}_{\text{LUMO}} = (\text{E}_g + \text{E}_{\text{HOMO}})$ , where the bandgap energy ( $\text{E}_g$ ) was estimated from the UV–Vis absorption data, following a method typically used for polymeric materials [54].

The thickness of the emission layer was obtained using Dektak Profilometer equipment, with a  $12.5$   $\mu\text{m}$  Stylus tip (Bruker). For this purpose, the films were deposited as performed for the devices, and a line

**Table 1**

Polycondensation results of conjugated copolymers, yield, molar mass ( $M_n$  and  $M_w$ ), dispersity ( $\bar{D}$ ), and  $^1\text{H}$  NMR signals.

Copolymer	Yield (%)	$M_n \times 10^3$ (g/mol)	$M_w \times 10^3$ (g/mol)	$\bar{D}$
F8BT-M	72	32.05	67.60	2.10
PFT	68	3.87	11.64	3.00
PFT-M	82	5.50	9.19	1.67
PFT-ME	74	8.74	20.15	2.30

was made to provide a step for the measurement.

### 2.4. PLED Assembly and characterization

As a light-emitting layer, PLED devices containing synthesized F8BT-M as well as PFT, PFT-M, and PFT-ME were assembled with the following configuration: glass-ITO | PEDOT:PSS | PVK | Polymer Light Emitting Layer | Ca | Al. For the sake of comparison and to have a reference device based on a polymeric material with a previously known response, a device of the same structure, but with the commercial F8BT as an emitting layer, was assembled and evaluated. All diodes were assembled as follows. First, glass-ITO substrates were photolithographed, cut, and cleaned. Then, a PEDOT:PSS (HTL) layer was deposited by spin-coating (3000 rpm, 40 s) and dried on a heating plate at  $120$   $^\circ\text{C}$  for 20 min in a Mbraun glovebox. Finally, the complementary HTL layer PVK (commercial) was deposited at a speed of 3000 rpm for 40 s in spin-coating above the PEDOT:PSS layer. For the formation of green emitter layers, materials solutions were obtained after weighing 10 mg of samples of thiophene copolymers, benzothiadiazole copolymers, and commercial F8BT, respectively, which were subsequently dissolved in 1 mL of tetrahydrofuran (THF). Before deposition, the solutions were filtered through a PTFE membrane filter (Millipore®, 0.45  $\mu\text{m}$ ). After spin-coating at 2000 rpm for 40 s, the films were annealed on a hot plate at  $100$   $^\circ\text{C}$  for 10 min. Finally, Ca (20 nm) and Al (80 nm) were thermally evaporated under  $5 \times 10^{-6}$  mbar inside an MBraun glovebox.

After assembling the PLED devices, they were transferred from the glovebox to a hermetically sealed sample holder for electrical characterization. The current-voltage curves were obtained with a Keithley 2410-C source meter. The electroluminescence (EL) spectra were acquired with an Ocean Optics USB2000+ portable fluorimeter, and the luminance and CIE coordinates were obtained with a color and luminance meter CS-100A (Konica Minolta). To limit the maximum current flowing to the diodes and thus prevent damage to the samples and contacts, scanning voltage was applied until 16 V. Therefore, the EL curves presented here are the result of an evaluation of voltages that provided some information on electroluminescence intensity under a maximum of 10V.

## 3. Results and discussion

### 3.1. Structure and molar mass

The copolymer samples were subjected to GPC and  $^1\text{H}$  NMR analyses. Table 1 summarizes the main results of the polycondensation and the yields obtained in the synthesis. Polymerization yields of around 70 % were obtained, and as the synthesis was carried out in the presence of Aliquat 336, higher  $M_w$  was achieved.

Overall, it is observed that carrying out the copolymerization in the presence of Aliquat 336 caused a gain in  $M_w$ . When observing Table 1, the copolymer F8BT-M (with the action of Aliquat 336) showed  $M_n$  of 32052 g/mol, a value higher than those previously reported [14,33, 47–49], as well as higher than the commercial F8BT used ( $M_n < 25000$  g/mol). Thus, the synthesized copolymer may have a longer conjugation length of alternating electron donor (fluorene) and acceptor (benzothiadiazole) portions in the polymer chain.

The idea in this work is to use F8BT-M as an emitting layer in light-

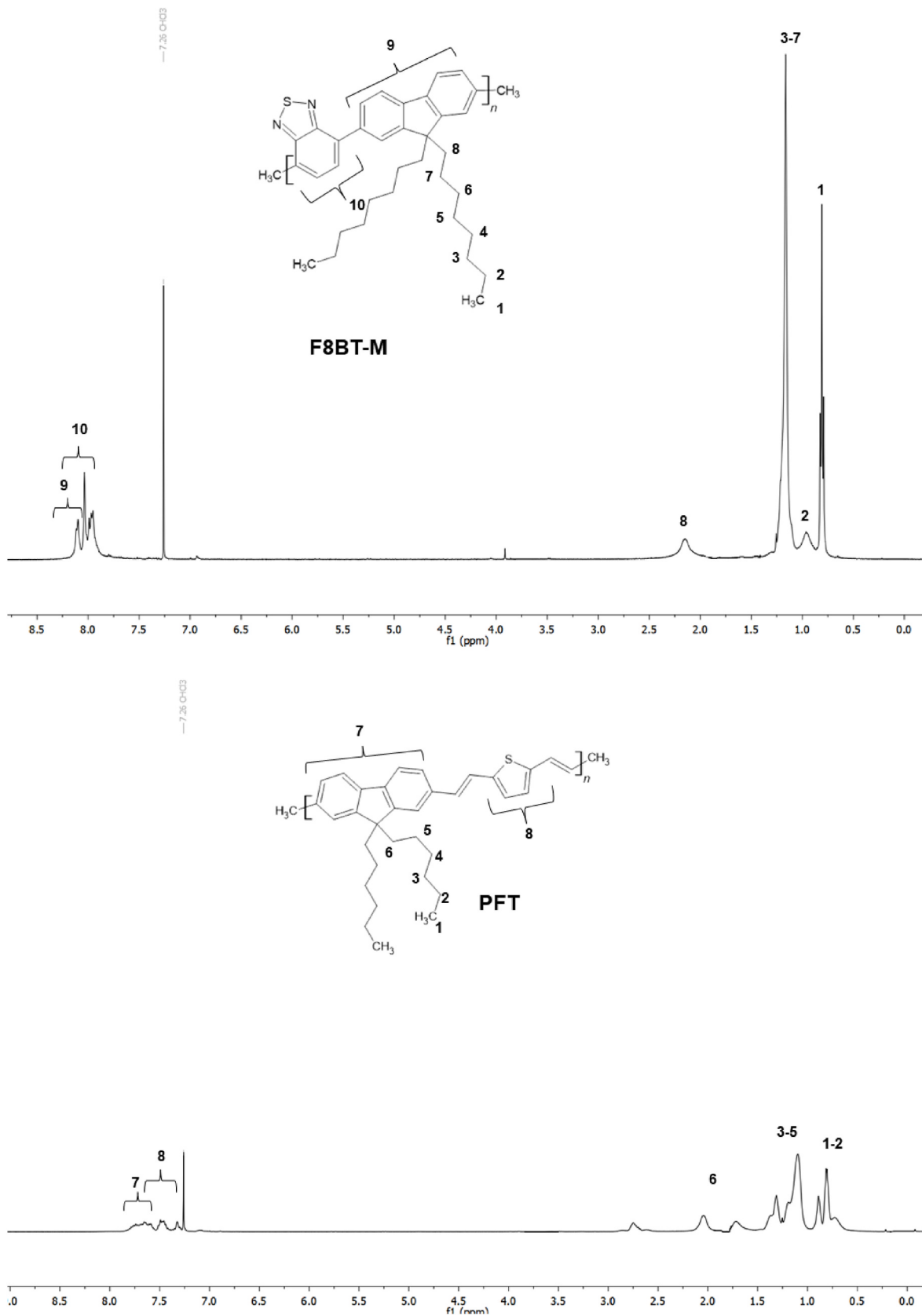


Fig. 3. <sup>1</sup>H NMR spectra of polymers F8BT-M, PFT, PFT-M and PFT-ME.



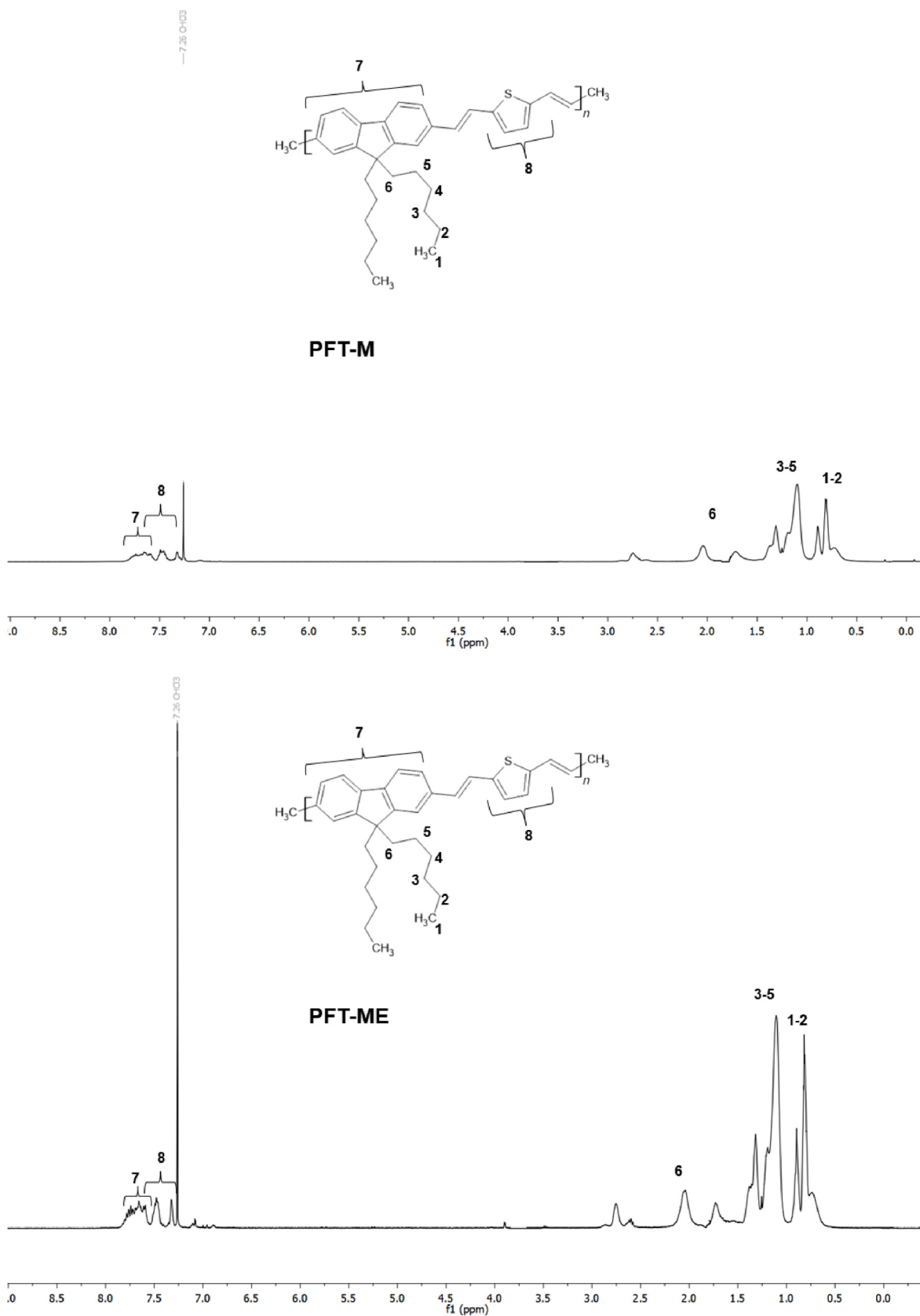


Fig. 3. (continued).

emitting devices. However, its use in other sections of the device is not disregarded. Suh et al, [55] report the synthesis of F8BT without Aliquat 336 as a precursor for a polyelectrolyte based on this copolymer. After

replacing the borolane group at the end of the copolymer with Br (F8BT-Br) for additional syntheses, the  $M_w$  achieved was 9916 g/mol. In this way, the relevance of using Aliquat 336 in obtaining higher  $M_w$  is

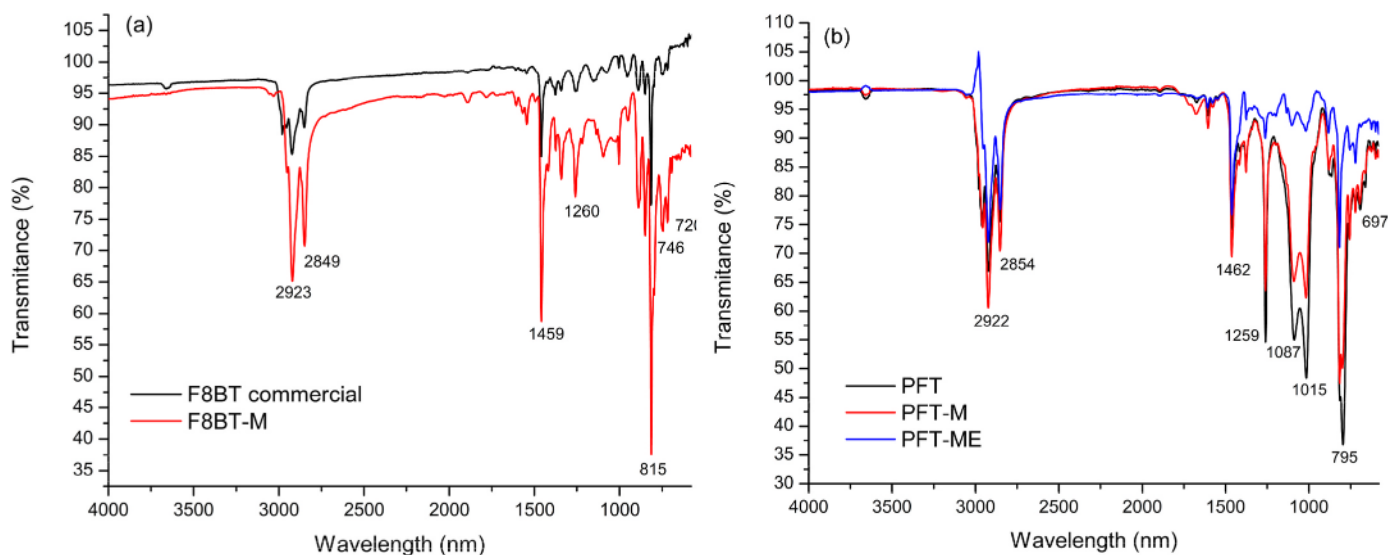


Fig. 4. FTIR spectra for (a) F8BT commercial and F8BT-M (b) PFT, PFT-M and PFT-ME copolymers.

observed. Indeed, by the methodology used here, it was possible to improve the properties in view of the greater conjugation that the polyelectrolyte would possess. This makes it possible the future, investigation of this aspect and its use as an electron transport layer (ETL) as done by the cited authors.

Aliquat 336 positively influenced the reduction in  $\bar{D}$  of the synthesized PFT copolymers since the sample obtained without this agent presented a  $\bar{D}$  of 3.00, while those obtained in the presence of this phase transfer catalyst resulted in lower  $\bar{D}$  values (PFT-M:  $\bar{D} = 1.67$  and PFT-ME:  $\bar{D} = 2.30$ ) [43]. A low  $\bar{D}$  implies that the chains have more regular sizes between them, so the closer  $\bar{D}$  is to one, the polymer chains have similar sizes. Notably, when Aliquat 336 was added to the reaction medium, this agent greatly influenced the  $M_n$  of the obtained copolymer (PFT-M) compared to the PFT material synthesized without Aliquat 336 (PFT). In addition, an increase in  $M_w$  was also verified with a longer reaction time of 60 h when the PFT-ME copolymer was produced. The greatest gain obtained was the decrease in  $\bar{D}$  with the use of Aliquat 336 since the sample without PFT presents higher  $\bar{D}$  and those obtained with this interfacial agent provided lower  $\bar{D}$ , even with larger chain sizes. It is well known that polymers with higher  $M_w$  generate positive effects on device efficiency. Moreover, the decrease in  $\bar{D}$  reduces structural defects in the polymer that affect energy transfer and charge retention/recombination, resulting in greater exciton generation, as well as higher

charge carrier mobilities.

The GPC curves are shown in Figure S1 (Supplementary data) for all synthesized materials. As seen in Table 1, the sample produced with Aliquat 336 in the reaction medium, synthesized with the longest, 60h, reaction time for the PFT-ME, has the highest average molar mass ( $M_n$ ) of 8743 g/mol.

All copolymers synthesized with the addition of Aliquat 336 exhibited  $M_w$  higher than those reported in the literature (between 4000 and 8000 g/mol) [13,50], demonstrating that this phase transfer catalyst provided greater uniformity in the coupling of the meres and consequently improved the properties of the obtained materials [42]. For the PFT series of copolymers, the sample synthesized in the dark with Aliquat 336 with a longer reaction time, PFT-ME, showed the highest  $M_n$  and  $M_w$  of the series. The increase in  $M_w$  with a longer reaction time is typical of Suzuki-Miyaura coupling reactions [56,57]. Such reactions have the advantage of less severe synthesis conditions and a very small catalytic amount, as used in the present work [58–60]. The reaction times used in these couplings generally range from 24 to 72 h, and regioregular polymers with a 25–50 kg/mol molar mass are obtained [48].

As for the polymeric structures of the F8BT and PFT copolymers, from the  $^1\text{H}$  NMR results shown in Fig. 3, it is observed that the polymeric structures estimated from the results are in good agreement with

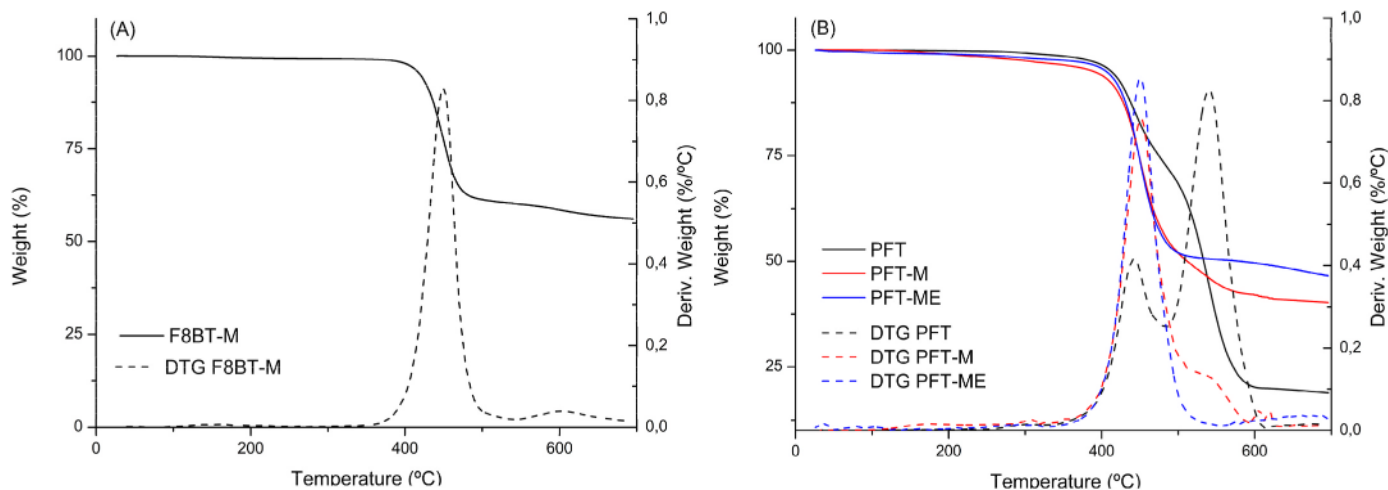


Fig. 5. Thermogravimetric analysis of the copolymers of (a) fluorene and benzothiadiazole and (b) fluorene and thiophene.

**Table 2**

Data from the thermogravimetric curves of fluorene copolymers with benzo-thiadiazole (F8BT) and fluorene-thiophene (PFT).

Copolymer	T <sub>10</sub> % (°C)	T <sub>onset</sub> (°C)	T <sub>max</sub> (°C)	Residue (%)
F8BT-M	432.3	424.4	449.1	5.6
PFT	431.4	408.1	539.1	1.8
PFT-M	421.3	419.3	450.9	4.0
PFT-ME	425.9	420.8	450.3	4.6

the spectrum obtained. The chemical shifts obtained were similar to those reported in the literature, concluding that F8BT was obtained with high purity. For PFT-based copolymers, the deuterated chloroform signal appears at a displacement of 7.28 ppm.

The data achieved are similar to those published by CHARAS et al. [11]; therefore, this copolymer was obtained with high purity, even with an interfacial agent in the reaction medium [11,17,33,48,61].

The structure of the copolymers was also evaluated using Fourier transform infrared spectroscopy (FTIR) analysis; the data obtained are shown in Fig. 4.

In Fig. 4 (a), the characteristic bands of the F8BT copolymer are presented; at 2923 and 2849 cm<sup>-1</sup>, there is the CH stretching; at 1260 and 1459 cm<sup>-1</sup> are bands corresponding to the vibrations of the HCC and HCH groups, while the band that extends at 720 and 746 cm<sup>-1</sup> indicate the presence of CCC and NCC [62,63] in the spectrum presented in Fig. 4 (b), which corresponds to PFT copolymers. The bands at 2922 and 2854 cm<sup>-1</sup> correspond to CH stretching to CH<sub>2</sub> (asymmetric and symmetric, respectively), while at 1462 cm<sup>-1</sup>, it is associated with vibrations of the fluorene rings, at 1259 cm<sup>-1</sup> with the CH bending of the thiophene and fluorene ring, at 1087 cm<sup>-1</sup> at CH curvature of the thiophene ring. Finally, the stretching at 795 cm<sup>-1</sup> corresponds to the C–S–C deformation of the thiophene ring [51].

### 3.2. Thermal properties

Fig. 5a shows the TG/DTG curves of the F8BT-M sample, where a single temperature of maximum mass loss (T<sub>max</sub>) is observed around 449 °C, which agrees with what is reported in the literature [64]. Data associated with the TG curves are compiled in Table 2.

The TGA of thiophene-coupled fluorene copolymers showed good thermal stability for all synthesized samples since they began to degrade at temperatures above 400 °C, as seen in Fig. 5b. The temperature at the

maximum degradation rate is around 450 °C for materials synthesized under the action of Aliquat 336, a temperature much higher than that reported by Pal et al. [13], where the degradation temperature was around 326 °C. Moreover, the higher amount of residue at 700 °C for the materials produced in the presence of Aliquat 336 compared with the polymer obtained in the absence of this agent, PFT, might be due to the higher M<sub>w</sub> attained. The TGA pyrolysis of polymers, PFT-M and PFT-ME, which have higher M<sub>w</sub>, hinders the evolution of decomposition gases, producing more char residue than the PFT sample.

### 3.3. X-ray diffraction

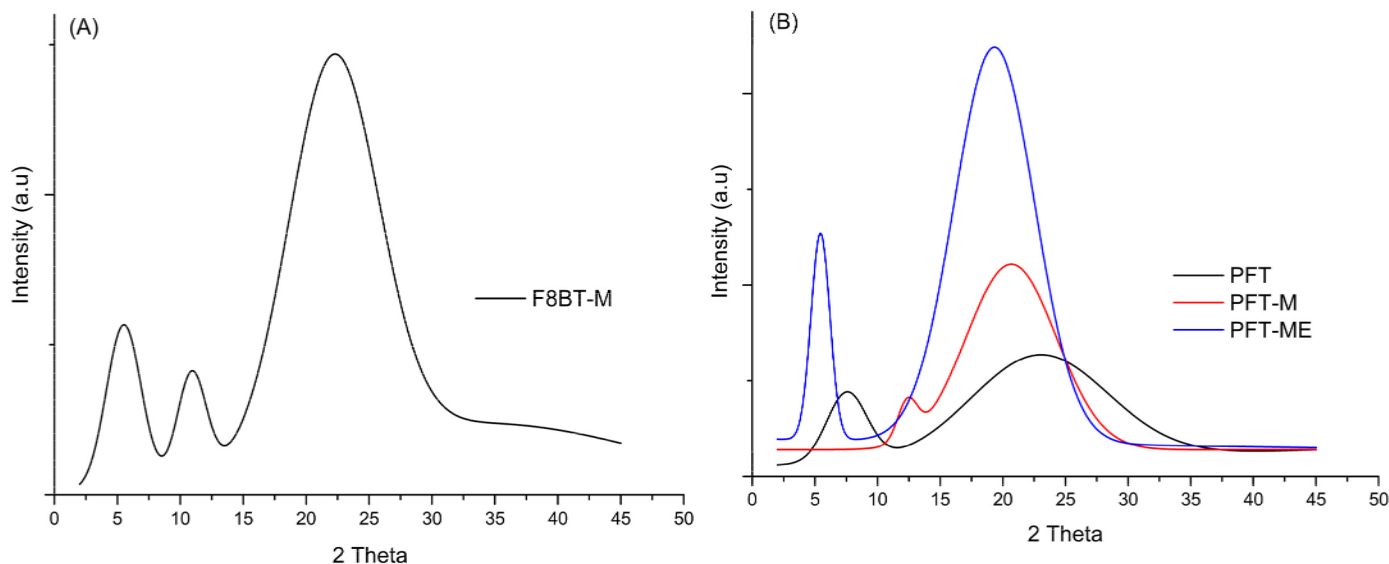
For the F8BT-M sample, the XRD curve in Fig. 6 presents three peaks at 5.5°, 10.9°, and 22.1°. Tanaka et al. [65] reported that for the F8BT material, XRD peaks are expected at 5.25° and 6.0°, associated with interplanar spacings of 16.9 and 14.7 Å, respectively. Such peaks correspond to the (001) and (100) crystallographic planes. The peak at about 22.1° corresponds to the (004) plane associated with the π-π stacking, for which the copolymer domains form monocyclic unit cells [23,66]. The structural ordering, transition temperature, and electrical properties of F8BT are functions of its M<sub>w</sub> [23]. That explains why the diffractions were less intense in the film produced in the present work. The M<sub>w</sub> is lower, and the material is predominantly amorphous, which agrees with what is reported in the literature [67].

For samples referring to thiophene copolymers, each curve has two halos, centered at 2θ = 7.6 and 23.2° for PFT, 12.5 and 20.6° for PFT-M, and 5.4 and 19.3° for PFT-ME, as presented in Table 3. Thus, the angles between 5 and 12° refer to the spacing between the main polymeric chains, while 20° is attributed to the π-π stacking spacing. The PFT-ME sample, the copolymer with the highest M<sub>w</sub>, has a greater interplanar distance than the other fluorene-thiophene materials. This observation may be linked to a lower packing of the polymeric chains due to its

**Table 3**

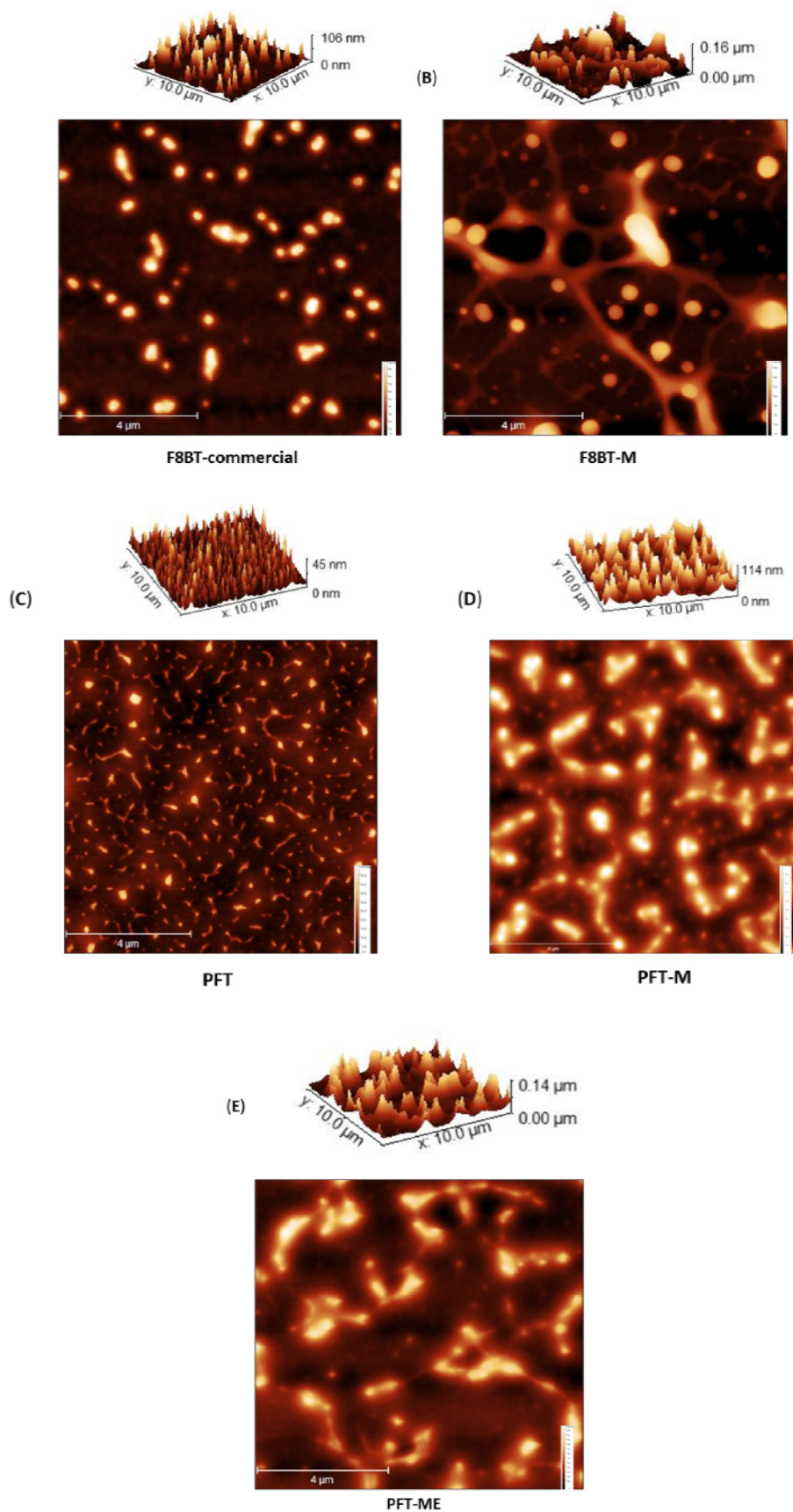
Data of X-ray diffractograms of the copolymers of F8BT-M, PFT, PFT-M, and PFT-ME.

Entry	2θ (°)	d (nm)
F8BT-M	5.5; 10.9; 22.1	1.60; 0.81; 0.40
PFT	7.6; 23.2	1.16; 0.38
PFT-M	12.5; 20.6	0.70; 0.43
PFT-ME	5.4; 19.3	1.63; 0.45



**Fig. 6.** X-ray diffraction curves of green-emitting copolymers based on (a) fluorene and benzo-thiadiazole and (b) fluorene and thiophene. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)





**Fig. 7.** AFM analysis of films of green light emitting copolymers: (a) commercial F8BT (b) F8BT-M (synthesized) (c) PFT (48 h without Aliquat 336) (d) PFT-M (48 h with Aliquat 336) (e) PFT-ME (60 h with Aliquat 336 in the dark). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

**Table 4**  
Roughness data obtained by AFM of the green light-emitting copolymers.

Samples	Ra (nm)	RMS (nm)
F8BT commercial	19.92	20.40
F8BT-M	29.52	33.46
PFT	15.37	7.35
PFT-M	16.83	6.28
PFT-ME	26.26	9.96

greater conjugation [38].

### 3.4. Atomic force microscopy (AFM)

Fig. 7 shows AFM height images of thin films of green light-emitting polymer materials.

Data related to the mean roughness (Ra) and mean square roughness (RMS) of the samples are shown in Table 4. This table shows that for the green light-emitting copolymers based on fluorene and benzothiadiazole units, the RMS of the synthesized sample was superior to the commercial polymer. Yamaguchi et al. [68] reported that the surface becomes rougher as the  $M_w$  increases, which would agree with what was observed for the synthesized samples since they presented higher molar mass when using Aliquat 336 in the reaction medium.

Such an effect was also observed for the green materials based on fluorene-thiophene. The PFT-ME sample, obtained in the presence of Aliquat 336, had a higher  $M_w$  than PFT, synthesized without this agent in the reaction medium. In addition, when performing such synthesis with the agent and in a longer reaction time of 60 h, the  $M_w$  was superior to the polymer PFT-M obtained for 48 h. The roughness of the polymeric film analyzed by AFM revealed that this property was correlated with the  $M_w$  obtained. Yamaguchi et al. [68] reported that the roughness depends on the  $M_w$  or aggregate size. Thus, surface roughness is not a statistical effect of polymer solubility, but comes from polymer structures when forming films. The influence of  $M_w$  on film roughness was also observed in Xiao et al. [69], who studied the effect of the  $M_w$  of copolymers on solar cell performance. They reported that the RMS increased as the molar mass increased, which may be associated with the random orientation of the polymer backbone.

### 3.5. UV-vis absorption spectra and fluorescence lifetime

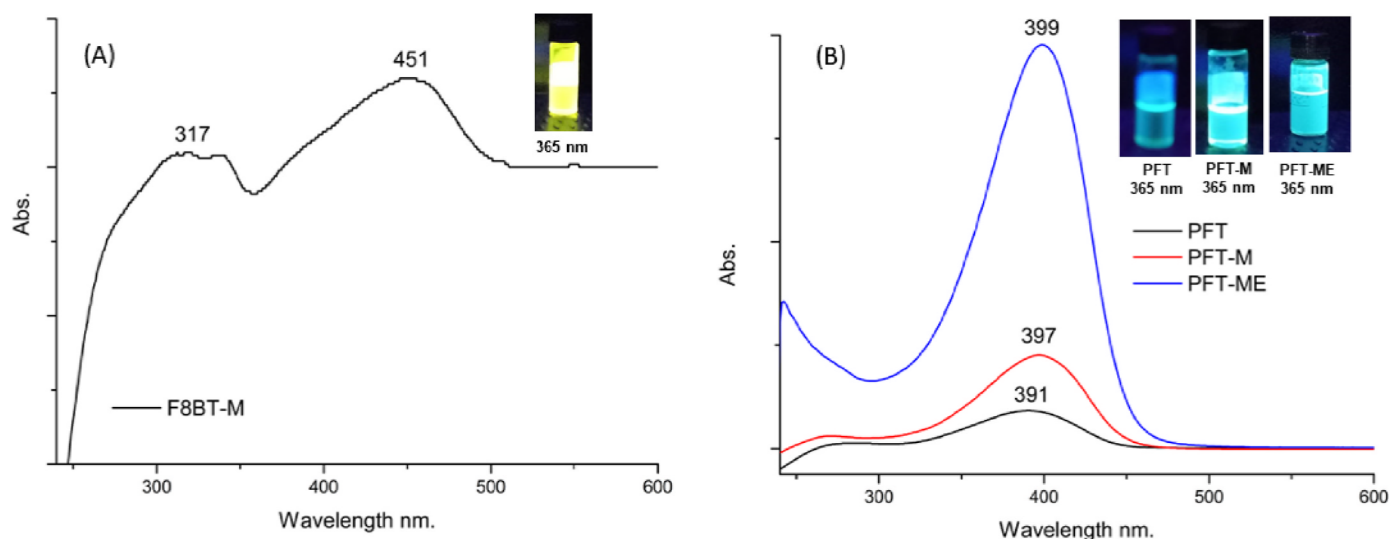
The F8BT-M sample was diluted in chloroform and then subjected to

UV-Vis absorption spectroscopy, displaying two electronic absorption bands. The higher energy band is placed around 317 nm and the lower one around 451 nm, which correspond to the fluorene unit (electron donor) and benzothiadiazole (acceptor), respectively, as seen in Fig. 8, in agreement with the literature [48]. The UV-vis spectroscopy curve of the commercial F8BT material is presented in Figure S2 of the Supplementary data. Solvatochromic measurements were performed to investigate the absorption and emission bands of the F8BT-M sample in several solvents. For this purpose, the sample was diluted in nine different solvents (acetone dichloromethane, dimethylformamide, dimethyl sulfoxide, ethane, methanol tetrahydrofuran, toluene and chloroform). According to this experiment, it was possible to note that the absorption peak varies from 450 to 467 nm, and the emission peak varies from 526 to 545 nm, depending on the solvent polarizability. In addition, the Stokes shift is of the order of 75 nm.

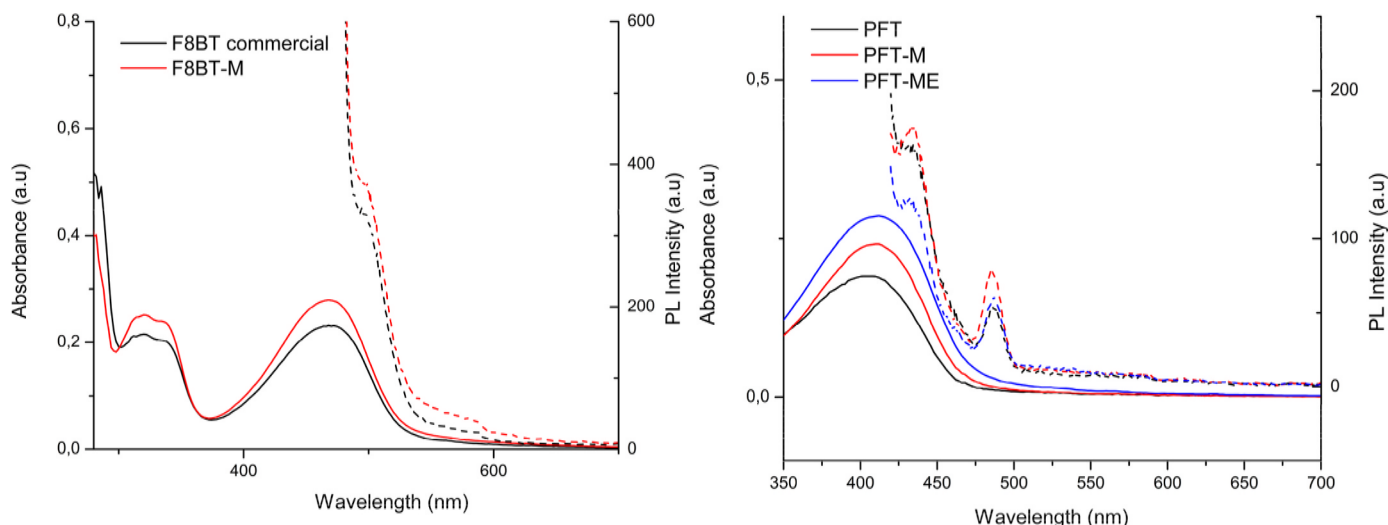
The time-resolved fluorescence technique [70] was employed to determine the F8BT-M fluorescence lifetime in chloroform solution. This technique is based on exciting the samples and monitoring the fluorescence signal perpendicularly to excitation. The third harmonic (343 nm) of an amplified femtosecond laser system (Pharos—Light Conversion, 1030 nm, 190 fs, 7.5 kHz) operating at 300 Hz was employed to excite the sample. The fluorescence signal is collected by a photodetector (800 ps of resolution) and acquired by a digital oscilloscope (3 GHz). More details of this technique can be found at [70–72]. The sample present monoexponential decay of  $3.0 \pm 0.3$  ns (See Figure S3 of the Supplementary data).

For the PFT copolymer, a  $\pi-\pi^*$  transition band has been reported around 398 nm (in chloroform solution) [26]. For the PFT synthesized without Aliquat 336, the absorption is found at 389 nm. For the materials synthesized in the presence of the phase transfer catalyst, PFT-M and PFT-ME, the absorbances appeared at 397 and 399 nm, respectively. A small redshift, around 10 nm, was observed in the PFT-ME sample and may be related to the increase in the  $\pi$  conjugated system due to the higher  $M_w$  [50].

The colors of the polymeric solutions in chloroform and their respective emission in a darkroom under the excitation of a UV lamp are demonstrated in the UV-Vis spectra shown in Fig. 8. In this way, it is possible to predict the color that will be emitted by the PLEDs containing these materials. In this sense, for the F8BT-M copolymer, there is a yellowish-green emission, and for the PFT copolymers, the emission is bluish-green, which corroborates the higher bandgap of PFT-ME. It is believed that with a longer annealing treatment allowing the rearrangement of the polymer chains, the efficiency of this material could be



**Fig. 8.** UV-Vis absorption spectra of the copolymers of (a) F8BT and (b) PFT samples. The inset shows photos of the samples diluted in chloroform (1mg/3 mL) in a darkroom under a 365 nm UV lamp.



**Fig. 9.** Absorption and emission spectrum curves of the green copolymer films in chlorobenzene (a) F8BT commercial and F8BT-M (emission when excited at 460 nm) (b) PFT without Aliquat 336 and PFT copolymers of different molar masses (emission when excited at 400 nm). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

**Table 5**

Photophysical and electrochemical properties of copolymers based on fluorene-alt-benzothiadiazole (F8BT-M) compared with commercial sample and fluorene-alt-thiophene (PFT, PFT-M, and PFT-ME).

Entry	UV-Vis in solution		UV-Vis in film		CV		
	$\lambda_{\text{max}}^{\text{sol}}$ (nm)	$\epsilon$ (L/mol.cm)	$\lambda_{\text{max}}^{\text{film}}$ (nm)	$\lambda_{\text{PL}}$ (nm)	$E_{\text{g}}^{\text{opt}}$ (eV) <sup>a</sup>	HOMO (eV) <sup>b</sup>	LUMO (eV) <sup>b</sup>
F8BT commercial	319; 450	–	320; 468	495; 573	2.35	–5.86	–3.51
F8BT-M	317; 451	100; 600	322; 468	497; 580	2.36	–5.86	–3.51
PFT	391	2920	404	432; 487	2.38	–5.62	–3.24
PFT-M	397	7240	410	435; 485	2.35	–5.59	–3.24
PFT-ME	399	31260	412	431; 487	2.68	–5.64	–2.96

<sup>a</sup> Estimated from the absorption onset collected from the UV-vis spectra of the films.

<sup>b</sup> Estimated from the cyclic voltammetry.  $E_{\text{HOMO}} = -(4.8 + E_{\text{onset}}^{\text{ox}})$  [eV].  $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g}}^{\text{opt}}$  [eV].  $E_{\text{g}}^{\text{opt}} = 1240/\lambda$  (nm).

increased. Fig. 9 shows the absorption and emission curves of the green copolymer films in the solvent chlorobenzene. The data obtained are presented in Table 5, where it is observed that the absorptions of the polymeric films are shifted to greater lengths. The main absorption band located at 468 nm for F8BT copolymers is associated with transitions of  $\pi$ - $\pi^*$  electrons and  $\pi$ -delocalized electrons along the chain, mainly along the fluorene unit (F8) [73–75]. The photoluminescence (PL) intensity is around 573–580 nm and may be related to the recombination of lower energy excitons from the excited state to the vibronic ground state [67, 76].

Pal et al. [77] report for the PFT copolymer a maximum absorption of 390 nm in film form in THF, while its PL is observed at 470 nm. Saeki et al. [78] report maximum absorption ( $\lambda_{\text{max}}$ ) of 420 nm and  $\lambda_{\text{PL}}$  of 469 nm in chloroform. The curves corresponding to the investigated novel copolymers showed maximum absorption values of 404 nm for PFT, 410 nm for PFT-M and 412 nm for PFT-ME. Such values are associated with the  $\pi$ - $\pi^*$  transition. The shift to longer wavelengths observed for the films produced is due to the large  $\pi$ - $\pi$  interaction of the condensed matter.

The onset absorptions observed in the UV-Vis spectra were used to calculate the  $E_{\text{g}}$ . This information is displayed in Figure S4 (Support Information). The  $E_{\text{g}}$  can be deduced by extrapolating the spectral tilt between 350 and 500 nm. The calculated values are presented in Table 5. For comparison, it summarized the data reported by other authors [48,79,80] for the F8BT copolymer (see Table S1- Supplementary data).

Fig. 10 presents the voltammograms of the green emitting materials reported here. Considering the parameters in Table 5 and the results

obtained for the commercial F8BT (Sigma Aldrich,  $M_{\text{n}} < 25000$  g/mol), the voltammetric data for F8BT-M were similar to the commercial polymer and superior to those reported in the literature [48]. This demonstrates that the present methodology led to the formation of an F8BT copolymer with optimized properties, thus revealing its potential as an emitting layer of green PLEDs.

The solvatochromic measurements for PFT-M and PFT-ME are shown in Figure S5 (Supplementary data). Through these measures, the absorption peaks vary from 398 to 402 nm for PFT-M and from 401 to 411 nm for PFT-ME, according to the employed solvent. Regarding emission peaks, PFT-M shows peaks from 502 to 548 nm, and PFT-ME presents peaks from 502 to 534 nm. In addition, it is possible to note that the Stokes shifts for these samples are around 100–140 nm. The fluorescence lifetime was determined following the procedure of time-resolved fluorescence already described. For PFT-M and PFT-ME, the time decay is of the order of 800 ps, which limits the resolution of the employed experimental apparatus.

The methodology for synthesizing PFT was similar to that of Chen et al. [81]. The PFT copolymer was expected to have a similar optical feature. These can be seen in Table S2 (Supplementary data), as well as the values reported by Pal et al. [13] for the fluorene-thiophene copolymer.

As observed in Table 5, for the fluorene-thiophene materials synthesized under the same reaction time, without PFT and with Aliquat 336, PFT-M, the bandgap and HOMO/LUMO values were similar and higher than that reported by Chen et al. [81]. However, when synthesized in a longer reaction time, the bandgap presented a value of 2.68 eV, which is very near to that found by Pal et al. [13], whose value was

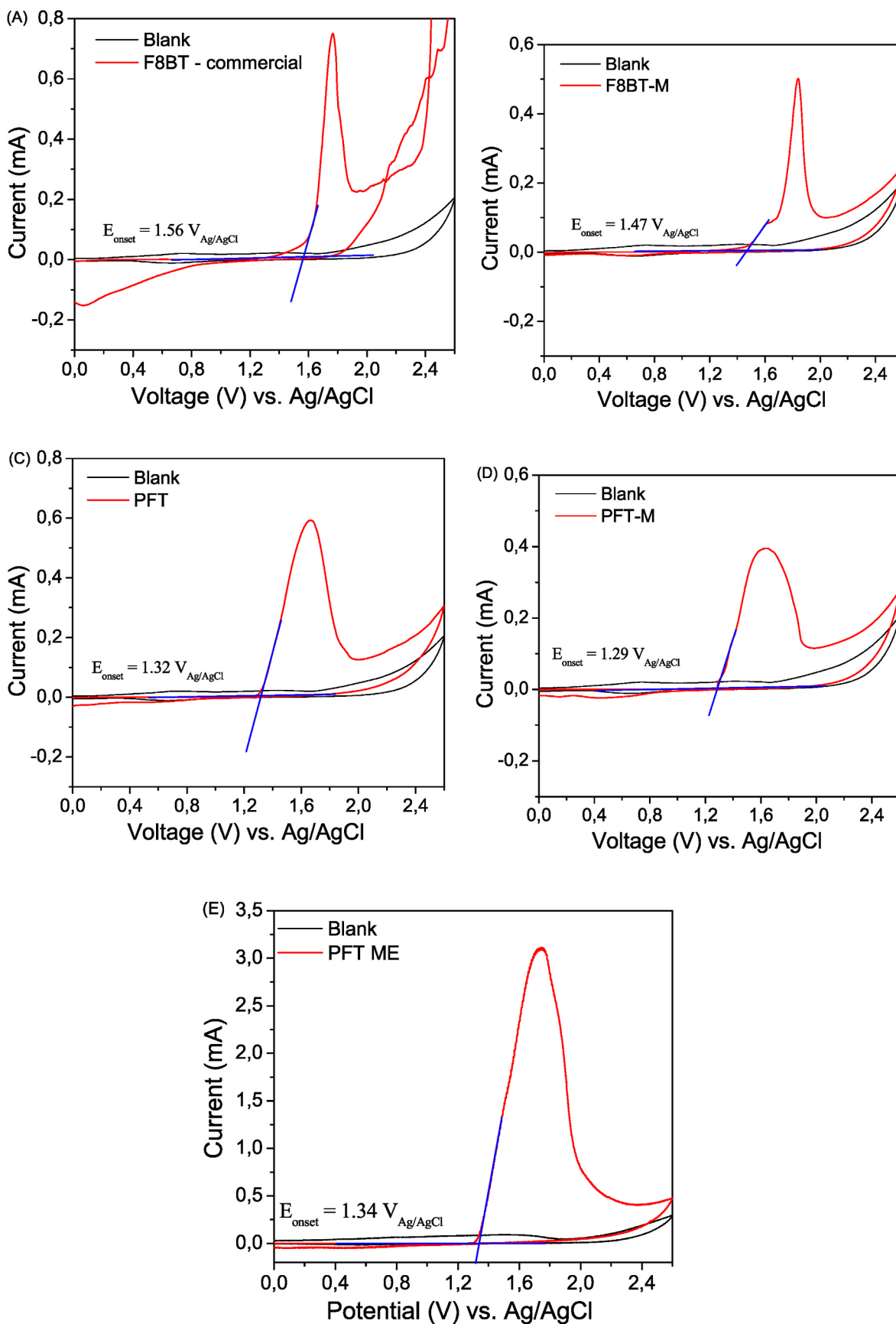


Fig. 10. CVs obtained for the green copolymers (a) commercial F8BT (b) F8BT-M (c) PFT (d) PFT-M and (e) PFT-ME. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



**Table 6**

Characteristics of PLEDs containing green light emitting copolymers as an electroluminescent layer.

EL layer	$\lambda_{\text{max}}^{\text{EL}}$ (nm)	$V_{\text{on}}$ (V)	$L_{\text{max}}$ (cd/m <sup>2</sup> )	$\eta_{\text{curr}}$ (mcd/A)	CIE (x,y)
F8BT (commercial)	521.5 (7.0 V)	4.0	210 (6.8 V)	55.4 (5.6 V)	(0.3210; 0.6539)
F8BT-M	522.8 (9.0 V)	4.8	327 (9.0 V)	132.6 (7.4 V)	(0.3203; 0.6563)
PFT-M	505.5 (10.0 V)	4.6	54 (9.8 V)	13.4 (6.0 V)	(0.2305; 0.466)
PFT-ME	489.0 (12.0 V)	4.8	168 (12.2 V)	19.75 (11.2 V)	(0.1998; 0.3865)

2.81 eV. Several factors influence the bandgap: (i) bond length alternation energy; (ii) aromatic resonance energy; (iii) twist angle; (iv) substituents; and (v) intermolecular interactions. Thus, incorporating thiophene portions in the polyfluorene structure allows the preparation of adjustable electroluminescent materials [28,82].

Table 5 also shows the extinction coefficients of the PFT copolymers synthesized at maximum absorption. It can be seen that greater values were achieved as the  $M_w$  increased and, consequently, the chain conjugation length increased. Plots of the extinction coefficient as a function of the wavelength are shown in Figure S6 of the Supplementary data.

### 3.6. Electroluminescence characteristics

By employing synthesized copolymers such as F8BT-M, PFT, PFT-M, and PFT-ME, a PLED device was constructed following the glass-ITO/PEDOT:PSS/PVK/Copolymer/Ca/Al configuration. A similar device was prepared for comparison with the commercial F8BT copolymer, a material with a well-known response, used as a reference [49,83]. The current-voltage-luminance curves are shown in Figure S7 (Supplementary data), and the parameters extracted from these curves are listed in Table 6. The complementary HTL layer of PVK was solubilized in THF, while the electroluminescent layers were in chlorobenzene. The thickness of each single polymer emitting layer deposited by spin-coating from chlorobenzene solutions was about 60 nm, as estimated with a Dektak profilometer.

The commercial F8BT showed a characteristic band in the EL spectra centered on the wavelength of 521 nm, whereas for the F8BT-M sample, the EL maximum is centered at 522 nm (Fig. 11). In both cases, the main emission band shows an increase in electroluminescence intensity when increasing the applied voltage from 5 to 9 V, which is similar to that reported by Zhong et al. [64], who developed a PLED device with the following configuration: ITO|PEDOT:PSS|PVK (40 nm)|polymer (80 nm)|CsF (1.5 nm)|Al (110 nm). It is similar to the present work, using a layer of PVK on top of the PEDOT:PSS layer, which was intended to improve the transport of holes to the active layer [64].

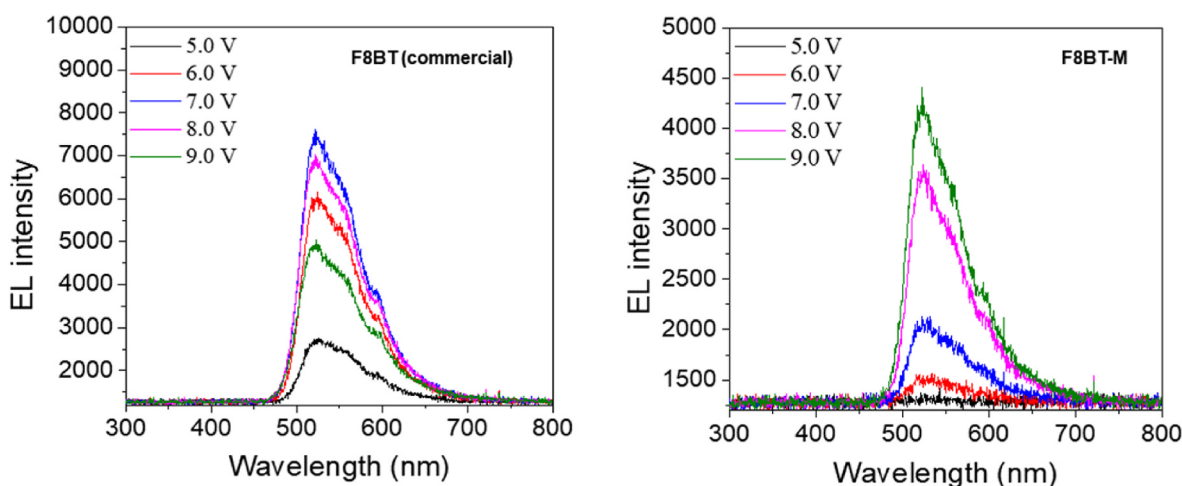


Fig. 11. EL spectra for the PLEDs: glass-ITO/PEDOT:PSS/PVK(commercial)/F8BT commercial or F8BT-M/Ca/Al.

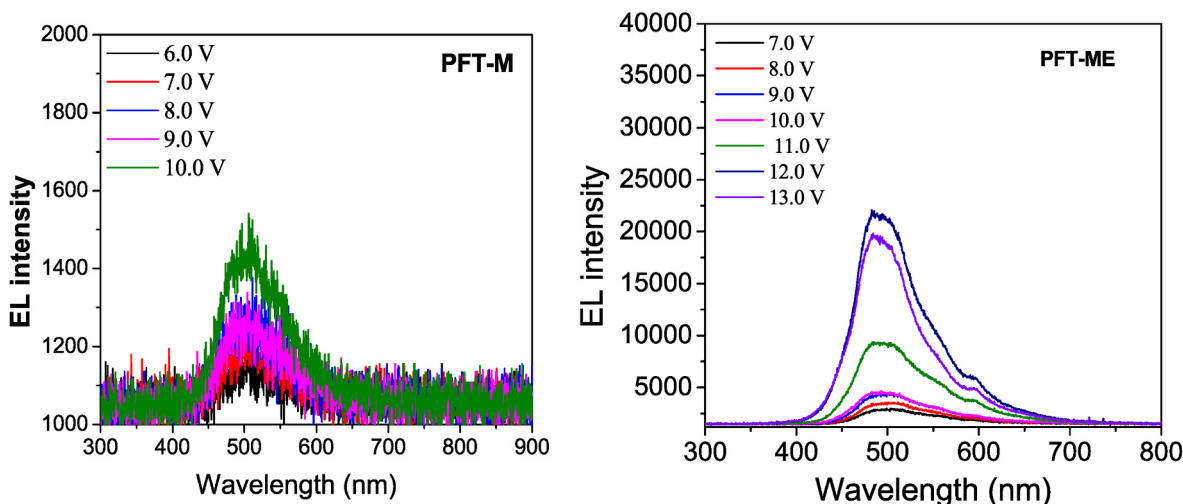
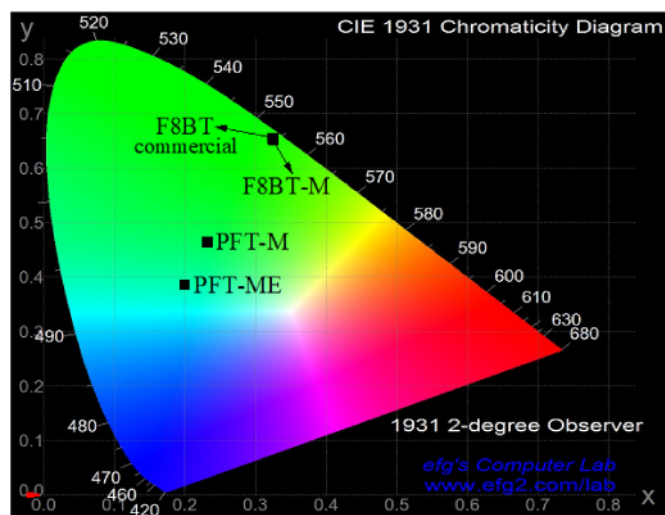


Fig. 12. EL spectra for the PLEDs: glass-ITO/PEDOT:PSS/PVK(commercial)/PFT-M or PFT-ME/Ca/Al.





**Fig. 13.** CIE chromaticity coordinates for the PLEDs composed of glass-ITO/PEDOT:PSS/PVK/F8BT commercial, F8BT-M, PFT-M, or PFT-ME/Ca/Al. These coordinates were obtained at the point of maximum luminance of each sample.

The EL profile of these samples resulted in emitted light with chromaticity coordinates of (0.3210; 0.6539) for commercial F8BT and (0.3203; 0.6563) for F8BT-M. Thus, the color emitted by both diodes was green. Overall, it was observed that the synthesized F8BT sample presents an emission similar to the commercial copolymer and is analogous to that reported in the literature [64,67]. However, it reaches even higher values of maximum luminance ( $L_{\max}$ ) and current efficiency ( $\eta_{\text{curr}}$ ) than the PLED containing the commercial sample evaluated in the same conditions, as displayed in Table 6.

The results of the green emitting device of F8BT-M can be compared to the work developed by Azevedo et al. [49] since they used the same type of device structure. Their device containing F8BT showed a turn-on voltage of 6 V and reached a maximum luminance of 123  $\text{cd}/\text{m}^2$  (at 9V). In contrast, the present device with F8BT-M had a turn-on voltage of 4.8 V and  $L_{\max}$  of 327  $\text{cd}/\text{m}^2$  (at 9V). It is noteworthy that the  $M_n$  of the F8BT material by Azevedo et al. [49] was around 22000–24000 g/mol, whereas F8BT-M with the use of Aliquat 336 has an  $M_n$  of 32000 g/mol, thus indicating that the molar mass probably influenced the electrical properties of the device. The higher drive voltage for the synthesized F8BT-M copolymer (4.8V) is associated with the greater roughness found for this film, possibly generating a greater energy barrier. Therefore, higher energy was needed to break it.

PFT copolymers have been the object of study because they present tunable EL when thiophene and thieno-arene groups are used in the main chain of the polymer [84–86]. In this way, the characteristics achieved for our investigated devices with different physicochemical properties from each other demonstrate the efforts to achieve characteristics superior to those already reported in the literature [77,78,87]. It also revealed their potential for the field of photonics. PLEDs were assembled with the following configuration: ITO/PEDOT:PSS/PVK/PFT, PFT-M, or PFT-ME/Ca/Al to investigate and compare the synthesized PFT copolymers.

The electroluminescence spectra of our novel PFT-based copolymers are shown in Fig. 12. It is possible to observe a single EL band centered at 505 nm for PFT-M and 488 nm for PFT-ME. These bands showed an electroluminescence intensity that rose when the applied voltage increased from 7 to 13 V. The current-voltage-luminance curves obtained for such devices are shown in Figure S5 (Supplementary data).

The PFT-based PLED did not show a measurable response using the available measurement setup. Therefore, no results from this PLED were obtained in the present work. This aspect may be related to the low  $M_w$

for PFT (3870 g/mol), which leads to poor film formation, as well as low solubility in chlorobenzene, resulting in thicknesses of less than 10 nm [88,89]. For the other devices, made with copolymers synthesized under the action of this phase transfer catalyst (PFT-M) and the one performed in the dark (PFT-ME), the results extracted from the characterization of the respective PLEDs are shown in Table 6. The data obtained for PFT-M were similar to that reported in the literature [90], reaching a maximum luminance of 54  $\text{cd}/\text{m}^2$  at 9.8 V.

As observed in Table 6, the material with the highest molar mass, PFT-ME, presented optimized electrical properties since the luminance achieved was almost 3 times greater than the sample synthesized in a shorter time and under light, with a trigger voltage similar to that of PFT-M. The EL profile of the PLED containing the PFT-M sample and the dark synthesized sample (PFT-ME) resulted in emitted light chromaticity coordinates of (0.2305; 0.466) and (0.1998; 0.3865), respectively, as can be seen in Fig. 13. The color of the light emitted by the PFT-M device was green, whereas that for the PFT-ME device was greenish-bluish. The synthesized PFT-M material presented a green light emission similar to that of the copolymer reported in the literature [90].

As for the F8BT-M polymer, the  $M_w$  obtained was higher than those mentioned in the literature [33,48], as well as higher than that of the commercial sample. This characteristic is possibly related to the improvement of electroluminescent properties when this material was used as an active layer in the light emitting device, compared to the commercial sample, showing a  $L_{\max}$  of 327  $\text{cd}/\text{m}^2$  and current efficiency of 132.6  $\text{mcd}/\text{A}$ , as seen in Table 6.

In view of this improvement in the properties of the F8BT-M device, future optimizations can be carried out based on molar mass and coupling syntheses and/or substitutions in order to transform this copolymer into a polyelectrolyte or a functionalized copolymer [55,91, 92] and also use it as an ETL for light-emitting devices. However, the results obtained so far serve as a guide for future work with this material.

The higher performance of PFT-ME is also closely related to its higher  $M_w$  (see Table 1) achieved through the action of the Aliquat 336 interface agent and a longer reaction time. The properties of the assembled devices revealed that this material was the one that could emit more light in the PFT-based copolymer series, presenting a  $L_{\max}$  of 168  $\text{cd}/\text{m}^2$ . Thus, their electrical properties have been shown to follow the improvements of the reaction medium used in the copolymer synthesis.

The thicknesses of the PFT copolymer films obtained by profilometry (see Fig. S8 of the Supplementary data) in the chlorobenzene solvent were less than 10 nm. As the electroluminescent properties are also dependent on thickness, they can, therefore, be improved by using another solvent to form the films, such as Toluene, in order to obtain thicknesses greater than 35 nm and, which might be associated with a better balance of charges [93,94].

#### 4. Conclusion

In this work, fluorene-benzothiadiazole and fluorene-thiophene based four green light-emitting polymeric materials, named F8BT-M, PFT, PFT-M, and PFT-ME, were successfully synthesized. It was observed that the reactions that contained the phase transfer catalyst Aliquat 336 allowed for optimizing the results for the copolymers, achieving greater thermal stability, with initial degradation temperature above 415 °C, high molar masses, and lower dispersity.

When these materials were employed in light-emitting devices, it was observed that elevating the molar mass of commercial resulted in higher luminance output from the device. F8BT-M ( $M_n > 32000$  g/mol). A polymer synthesized in the presence of Aliquat 336 presented a  $L_{\max}$  of 327  $\text{cd}/\text{m}^2$  compared to 210  $\text{cd}/\text{m}^2$  of commercial F8BT ( $M_n < 25000$  g/mol).

The polymer light emitting device (PLED) assembled with PFT did not present any optical-electrical signal detectable with our setup. However, the PFT-M and PFT-ME samples, both synthesized in the

presence of Aliquat 336, revealed maximum luminances around 54 and 168 cd/m<sup>2</sup>, respectively. The phase transfer catalyst agent was paramount in optimizing the synthesis conditions that directly influenced the properties of the materials and devices. According to the chromaticity diagram, all PLED devices showed the emission of green light, although with different green shades. Even though the results are not much significant, they demonstrate that the synthesis of copolymers and the optimization of the reaction medium are sufficient to change the photoelectric properties. Indeed, they can be improved with the use of dopants or the construction of more elaborate devices with blocking layers of electrons and holes, as well as the use of enhanced carrier injection layers.

### 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.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jmrt.2023.12.249>.

### References

- [1] Fang Z, Eshbaugh AA, Schanze KS. Low-bandgap donor-acceptor conjugated polymer sensitizers for dye-sensitized solar cells. *J Am Chem Soc* 2011;133:3063–9. <https://doi.org/10.1021/ja109926k>.
- [2] Zhu Y, Champion RD, Jenekhe SA. Conjugated donor-acceptor copolymer semiconductors with large intramolecular charge transfer: synthesis, optical properties, electrochemistry, and field effect carrier mobility of thienopyrazine-based copolymers. *Macromolecules* 2006;39:8712–9. <https://doi.org/10.1021/ma061861g>.
- [3] Carbas BB, Kivrak A, Kavak E. Electrosynthesis of a new indole based donor-acceptor-donor type polymer and investigation of its electrochromic properties. *Mater Chem Phys* 2017;188:68–74. <https://doi.org/10.1016/j.matchemphys.2016.12.040>.
- [4] Piravadi S, Doyranli C, Altınışık S, Bilgili H, Canımurkubey B, Koyuncu S. Fluorene-based donor-acceptor-type multifunctional polymer with bicarbazole pendant moiety for optoelectronic applications. *J Polym Sci* 2021;59:1829–40. <https://doi.org/10.1002/pol.20210221>.
- [5] Wang Y, Zhu Y, Xie G, Zhan H, Yang C, Cheng Y. Bright white electroluminescence from a single polymer containing a thermally activated delayed fluorescence unit and a solution-processed orange OLED approaching 20% external quantum efficiency. *J Mater Chem C* 2017;5:10715–20. <https://doi.org/10.1039/c7tc03769d>.
- [6] Leclerc M. Polyfluorenes: Twenty years of progress. *J Polym Sci Part A Polym Chem* 2001;39:2867–73. <https://doi.org/10.1002/pola.1266>.
- [7] Nirmani LPT, Pary FF, Nelson TL. Mechanochemical Suzuki polymerization for the synthesis of polyfluorenes. *Green Chem Lett Rev* 2022;1. <https://doi.org/10.1080/17518253.2022.2107406>. –6.
- [8] Shi WX, Liu N, Zhou YM, Cao XA. Effects of postannealing on the characteristics and reliability of polyfluorene organic light-emitting diodes. *IEEE Trans Electron Dev* 2019;66:1057–62. <https://doi.org/10.1109/TEDE.2018.2888858>.
- [9] Piravadi Mucur S, Kacar R, Meric C, Koyuncu S. Thermal annealing effect on light emission profile of polyfluorenes containing double bond subunit. *Org Electron* 2017;50:55–62. <https://doi.org/10.1016/j.orgel.2017.07.026>.
- [10] Kok C, Doyranli C, Canımurkubey B, Piravadi Mucur S, Koyuncu S. Effect of thiophene linker addition to fluorene-benzotriazole polymers with the purpose of achieving white emission in OLEDs. *RSC Adv* 2020;10:18639–47. <https://doi.org/10.1039/d0ra02527e>.
- [11] Charas A, Morgado J, Martinho JMG, Alcácer L, Lim SF, Friend RH, et al. Synthesis and luminescence properties of three novel polyfluorene copolymers. *Polymer (Guildf)* 2003;44:1843–50. [https://doi.org/10.1016/S0032-3861\(03\)00028-4](https://doi.org/10.1016/S0032-3861(03)00028-4).
- [12] Fujinami Y, Kuwabara J, Lu W, Hayashi H, Kanbara T. Synthesis of Thiofene- and Bithiophene- based alternating copolymers via Pd-catalyzed Direct C-H Arylation. *ACS Macro Lett* 2012;68:67–70.
- [13] Pal B, Yen WC, Yang JS, Chao CY, Hung YC, Lin ST, et al. Substituent effect on the optoelectronic properties of alternating fluorene-cyclopentadithiophene copolymers. *Macromolecules* 2008;41:6664–71. <https://doi.org/10.1021/ma800362n>.
- [14] de Moraes A, Duarte LGTA, Turchetti DA, Mendes RA, de Freitas JN, Atvars TDZ, et al. Synthesis and optical properties of a fluorene-benzothiadiazole anthracene copolymer. *Synth Met* 2022;283:116970. <https://doi.org/10.1016/j.synthmet.2021.116970>.
- [15] Al-Azzawi AGS, Dannoun EMA, Aziz SB, Iraqi A, Al-Saeedi SI, Nofal MM, et al. Synthesis and characterization of polymers containing Ethynylene and Ethynylene-thiophene based alternating polymers containing 2,1,3-linked Naphthothiadiazole Units as acceptor linked with fluorine as donor: electrochemical and spectroscopic studies. *Polymers* 2022;14. <https://doi.org/10.3390/polym14194139>.
- [16] Kabra D, Song MH, Wenger B, Friend RH, Snaith HJ. High efficiency composite metal oxide-polymer electroluminescent devices: a morphological and material based investigation. *Adv Mater* 2008;20:3447–52. <https://doi.org/10.1002/adma.200800202>.
- [17] Faria GC, Von Seggern H, Faria RM, Deazevedo ER. Influence of molecular dynamics on the dielectric properties of poly(9,9-di-n-octylfluorene-altbenzothiadiazole)-based devices. *IEEE Trans Dielectr Electr Insul* 2012;19:1181–5. <https://doi.org/10.1109/TDEI.2012.6259987>.
- [18] Lehnhardt M, Riedl T, Rabe T, Kowalsky W. Room temperature lifetime of triplet excitons in fluorescent host/guest systems. *Org Electron* 2011;12:486–91. <https://doi.org/10.1016/j.orgel.2010.12.017>.
- [19] Baycan Koyuncu F, Davis AR, Carter KR. Emissive conjugated polymer Networks with tunable band-Gaps via Thiol–Ene click chemistry. *Chem Mater* 2012;24:4410–6. <https://doi.org/10.1021/cm302790a>.
- [20] Davis AR, Carter KR. Controlling optoelectronic behavior in poly(fluorene) networks using thiol–ene photo-click chemistry. *Macromolecules* 2015;48:1711–22. <https://doi.org/10.1021/ma5014226>.
- [21] Zhang Y, Blom PWM. Electron and hole transport in poly(fluorene-benzothiadiazole). *Appl Phys Lett* 2011;98:2011–4. <https://doi.org/10.1063/1.3574907>.
- [22] Wang B, Ye H, Riede M, Bradley DDC. Chain conformation control of fluorene-benzothiadiazole copolymer light-emitting diode efficiency and lifetime. *ACS Appl Mater Interfaces* 2021;13:2919–31. <https://doi.org/10.1021/acsami.0c18490>.
- [23] Donley CL, Zaumseil J, Andreasen JW, Nielsen MM, Sirringhaus H, Friend RH, et al. Effects of packing structure on the optoelectronic and charge transport properties in poly(9,9-di-n-octylfluorene-alt-benzothiadiazole). *J Am Chem Soc* 2005;127:12890–9. <https://doi.org/10.1021/ja051891j>.
- [24] Roncali J. Conjugated poly(thiophenes): synthesis, functionalization, and applications. *Chem Rev* 1992;92:711–38. <https://doi.org/10.1021/cr00012a009>.
- [25] Le DT, Truong NTT, Luu TH, Nguyen L-T T, Hoang MH, Huynh HPK, et al. Donor-acceptor and donor–donor alternating conjugated polymers based on dithieno[3,2-b:2',3'-d]pyrrole: synthesis, optical properties and organic solar cells applications. *J Polym Res* 2022;29:111. <https://doi.org/10.1007/s10965-022-02969-9>.
- [26] Pasini M, Destri S, Porzio W, Botta C, Giovannella U. Electroluminescent poly (fluorene-co-thiophene-S,S-dioxide): synthesis, characterisation and structure-property relationships. *J Mater Chem* 2003;13:807–13. <https://doi.org/10.1039/b208742a>.
- [27] Yang R, Tian R, Hou Q, Zhang Y, Li Y, Yang W, et al. Light-emitting copolymers based on fluorene and selenophene - comparative studies with its sulfur analogue: poly(fluorene-co-thiophene). *J Polym Sci Part A Polym Chem* 2005;43:823–36. <https://doi.org/10.1002/pola.20562>.
- [28] Donat-bouillud A, Le I, Tao Y. Light-emitting diodes from fluorene-based. *Chem Mater* 2000;12:1931–6.
- [29] Piliccode N, Nk M, Acharya M, Naik P, Sm N, Adhikari AV. New blue light emitting cyanopyridine based conjugated polymers: from molecular engineering to PLED applications. *J Photochem Photobiol Chem* 2019;378:38–45. <https://doi.org/10.1016/j.jphotochem.2019.04.012>.
- [30] Nosova GI, Lypenko DA, Smyslov RY, Zhukova EV, Berezin IA, Litvinova LS, et al. Copolyfluorenes containing carbazole or triphenylamine and Diethoxyphosphoryl groups in the side chains as white-light-emitting polymers. *Polymer (Guildf)* 2020;210:122978. <https://doi.org/10.1016/j.polymer.2020.122978>.
- [31] Zou Y, Wang D, Guo J, Yang J, Pu Y, Chen J-F. Synthesis of poly(9,9-dioctylfluorene) in a rotating packed bed with enhanced performance for polymer light-emitting diodes. *Polym Chem* 2022;13:3506–12. <https://doi.org/10.1039/D2PY00297C>.
- [32] Sigl M, Rath T, Schlemmer B, Fürk P, Trimmel G. Synthesis of a fluorene and quinoxaline-based co-polymer for organic electronics. *Monatshfte Fur Chemie* 2023;154:543–51. <https://doi.org/10.1007/s00706-022-03030-7>.
- [33] Pedroso Silva Santos B, Candido L, Furtado JG de M, Ribeiro A de C, Valaski R, Marques M de FV. Random and block conjugated polymers: a comparative study of properties. *J Macromol Sci Part A Pure Appl Chem* 2020;57:363–78. <https://doi.org/10.1080/10601325.2019.1698966>.
- [34] Van Pruijsen GWP, Gholamrezaie F, Wien MM, Janssen RAJ. Synthesis and properties of small band gap thienoisindigo based conjugated polymers. *J Mater Chem* 2012;22:20387–93. <https://doi.org/10.1039/c2jm34668k>.
- [35] Yu CY, Godana AS. Conjugated polymer nanoparticles based on fluorenes, PEGylated carbazoles and diphenylamines. *Eur Polym J* 2018;99:165–71. <https://doi.org/10.1016/j.eurpolymj.2017.12.019>.
- [36] Yasa M, Arslan Udum Y, Toppare L. Effect of random copolymerization on the optical properties of selenophene and thieno[3,4-c]pyrrole-4,6-dione conjugated polymers. *Microchem J* 2022;178:107395. <https://doi.org/10.1016/j.microc.2022.107395>.

- [37] Do TT, Matsuki K, Sakanoue T, Wong FL, Manzhos S, Lee CS, et al. Indenofluorene-based-copolymers: influence of electron-deficient benzothiadiazole (BT) and benzoxadiazole (BO) moieties on light emitting devices. *Org Electron* 2019;70: 14–24. <https://doi.org/10.1016/j.orgel.2019.03.050>.
- [38] Santos BPS, Lima AB, De Araújo FL, Mota IC, Ribeiro ADC, Nogueira AF, et al. Synthesis of novel low bandgap random and block terpolymers with improved performance in organic solar cells. *J Mater Res Technol* 2021;10:51–65. <https://doi.org/10.1016/j.jmrt.2020.11.101>.
- [39] Park K, Shin EY, Jiao X, McNeill CR, Kim YH, Kwon SK, et al. Effect of backbone sequence of a naphthalene diimide-based copolymer on performance in n-type organic thin-film transistors. *ACS Appl Mater Interfaces* 2019;11:35185–92. <https://doi.org/10.1021/acsami.9b09607>.
- [40] Salazar E, Ortiz MI, Urtiaga AM, Irabien JA. Equilibrium and kinetics of Cr(VI) extraction with Aliquat 336. *Ind Eng Chem Res* 1992;31:1516–22. <https://doi.org/10.1021/ie00006a014>.
- [41] Resina M, Fontàs C, Palet C, Muñoz M. Comparative study of hybrid and activated composite membranes containing Aliquat 336 for the transport of Pt(IV). *J Membr Sci* 2008;311:235–42. <https://doi.org/10.1016/j.memsci.2007.12.018>.
- [42] Mikkola JP, Virtanen P, Sjöholm R. Aliquat 336®—a versatile and affordable cation source for an entirely new family of hydrophobic ionic liquids. *Green Chem* 2006;8:250–5. <https://doi.org/10.1039/b512819f>.
- [43] Zhou W, Wen Y, Ma L, Liu Y, Zhan X. Conjugated polymers of rylene diimide and phenothiazine for n-channel organic field-effect transistors. *Macromolecules* 2012; 45:4115–21. <https://doi.org/10.1021/ma3005058>.
- [44] Paul S, Islam MM, Islam SM. Suzuki-Miyaura reaction by heterogeneously supported Pd in water: recent studies. *RSC Adv* 2015;5:42193–221. <https://doi.org/10.1039/b000000x>.
- [45] Castanet AS, Colobert F, Desmurs JR, Schlama T. Biaryl synthesis via Suzuki coupling promoted by catalytic amounts of quaternary ammonium salts. *J Mol Catal Chem* 2002;182–183:481–7. [https://doi.org/10.1016/S1381-1169\(01\)00489-7](https://doi.org/10.1016/S1381-1169(01)00489-7).
- [46] Said K, Salem R Ben. Ultrasonic activation of Suzuki and Miyaura cross-coupling reactions catalyzed by palladium. *Adv Chem Eng Sci* 2016;6:111–23. <https://doi.org/10.4236/aces.2016.62013>.
- [47] Elmalem E, Kiriy A, Huck WTS. Chain-growth Suzuki polymerization of n-type fluorene copolymers. *Macromolecules* 2011;44:9057–61. <https://doi.org/10.1021/ma201934q>.
- [48] Wang L, Pan C, Liang A, Zhou X, Zhou W, Wan T, et al. The effect of the backbone structure on the thermoelectric properties of donor-acceptor conjugated polymers. *Polym Chem* 2017;8:4644–50. <https://doi.org/10.1039/c7py01005b>.
- [49] de Azevedo D, Freitas JN, Domingues RA, Faleiros MM, de Almeida Santos TE, Atvars TDZ. Tuning the emission color of a single-layer polymer light-emitting diode with a solution-processed external layer. *Synth Met* 2016;222:205–10. <https://doi.org/10.1016/j.synthmet.2016.10.024>.
- [50] Vamvounis G, Schulz GL, Holdcroft S. Enhanced blue-violet emission from poly (fluorene-co-thiophene). *Host-Guest Systems* 2004;7:8897–902.
- [51] Rodrigues R da R, de Aquino TP, Caseli L, Péres LO. Enzyme activity of thiophene-fluorene based-copolymer blended with urease in thin films. *Colloids Surfaces A Physicochem Eng Asp* 2020;603. <https://doi.org/10.1016/j.colsurfa.2020.125139>.
- [52] Zhu J, Wang J, Lu H, Qiu L. Solution-processed polarized light-emitting diodes. *J Mater Chem C* 2020;8:9147–62. <https://doi.org/10.1039/d0tc01639j>.
- [53] Moghe D, Kabra D. Polymer light-emitting diodes. Elsevier Inc; 2019. <https://doi.org/10.1016/B978-0-12-813647-8.00009-6>.
- [54] De Freitas JN, Pivrikas A, Nowacki BF, Akcelrud LC, Sariciftci NS, Nogueira AF. Investigation of new PPV-type polymeric materials containing fluorene and thiophene units and their application in organic solar cells. *Synth Met* 2010;160: 1654–61. <https://doi.org/10.1016/j.synthmet.2010.05.036>.
- [55] Suh M, Bailey J, Kim SW, Kim K, Yun DJ, Jung Y, et al. High-efficiency polymer LEDs with fast response times fabricated via selection of electron-injecting conjugated polyelectrolyte backbone structure. *ACS Appl Mater Interfaces* 2015;7: 26566–71. <https://doi.org/10.1021/acsami.5b07862>.
- [56] Nguyen TH, Nguyen L-TT, Hoang MH, Nguyen T-Q, Cu ST, Simada R, et al. Intramolecular catalyst transfer on N-acyl dithieno[3,2-b:2',3'-d]pyrroles in nonstoichiometric Suzuki-Miyaura polycondensation toward high molecular weight conjugated copolymers at room temperature. *Eur Polym J* 2023;186: 111867. <https://doi.org/10.1016/j.eurpolymj.2023.111867>.
- [57] Andrews MJ, Brunen S, McIntosh RD, Mansell SM. Preformed Pd(II) catalysts based on monoanionic [N,O] ligands for suzuki-miyaura cross-coupling at low temperature. *Catalysts* 2023;13.
- [58] ÇETİN A. Suzuki-Miyaura Coupling Polymerization: Synthesis, Characterization and Optical Properties. *İğdır Üniversitesi Fen Bilim Enstitüsü Derg* 2023;13: 494–503. <https://doi.org/10.21597/jist.1178152>.
- [59] Yakimanskiy AA, Kaskevich KI, Zhukova EV, Berezin IA, Litvinova LS, Chulkova TG, et al. Synthesis, photo- and electroluminescence of new polyfluorene copolymers containing dicyanostilbene and 9,10-dicyanophenanthrene in the main chain. *Materials* 2023;16:1–14.
- [60] Zhang K, Tkachov R, Ditte K, Kiriy N, Kiriy A, Voit B. AB- versus AA+BB-Suzuki polycondensation: a palladium/tris(tert-butyl)phosphine catalyst can outperform conventional catalysts. *Macromol Rapid Commun* 2020;41:1–6. <https://doi.org/10.1002/marc.201900521>.
- [61] Justino LLG, Luísa Ramos M, Abreu PE, Carvalho RA, Sobral AJFN, Scherf U, et al. Conformational studies of poly(9,9-dialkylfluorene)s in solution using NMR spectroscopy and density functional theory calculations. *J Phys Chem B* 2009;113: 11808–21. <https://doi.org/10.1021/jp902666e>.
- [62] Sultan Erkan. Theoretical and experimental spectroscopic properties and molecular docking of F8BT p-type semiconducting polymer. *Russ J Phys Chem A* 2020;94: 445–52. <https://doi.org/10.1134/S0036024420020314>.
- [63] Kim J, Chougale MY, Shaikat RA, Patil SR, Noman M, Patil CS, et al. F8BT-based highly sensitive humidity sensor for metaverse interfacing. *Sens Actuators, B* 2023; 398:134717. <https://doi.org/10.1016/j.snb.2023.134717>.
- [64] Zhong W, Liang J, Hu S, Jiang XF, Ying L, Huang F, et al. Effect of monofluoro substitution on the optoelectronic properties of benzo[c][1,2,5]thiadiazole based organic semiconductors. *Macromolecules* 2016;49:5806–16. <https://doi.org/10.1021/acs.macromol.6b00185>.
- [65] Tanaka H, Kajii H, Ohmori Y. Effects of molecular packing on the field-effect mobility and external quantum efficiency of ambipolar polymer light-emitting transistors incorporating a donor-acceptor polymer. *Synth Met* 2015;203:10–5. <https://doi.org/10.1016/j.synthmet.2015.02.008>.
- [66] Chu CW, Jeng KS, Chi MH, Tsai CC, Cheng MH, Chen JT. Confinement effects on the optical properties and chain conformations of poly(9,9-di-n-octylfluorene-alt-benzothiadiazole) nanotubes. *Macromol Chem Phys* 2016;217:2074–80. <https://doi.org/10.1002/macp.201600178>.
- [67] Mamada M, Komatsu R, Adachi C. F8BT oligomers for organic solid-state lasers. *ACS Appl Mater Interfaces* 2020;12:28383–91. <https://doi.org/10.1021/acsami.0c05449>.
- [68] Yamaguchi T, Yamazaki K, Namatsu H. Influence of molecular weight of resist polymers on surface roughness and line-edge roughness. *J Vac Sci Technol B Microelectron Nanom Struct* 2004;22:2604. <https://doi.org/10.1116/1.1805546>.
- [69] Xiao Z, Sun K, Subbiah J, Qin T, Lu S, Purushothaman B, et al. Effect of molecular weight on the properties and organic solar cell device performance of a donor-acceptor conjugated polymer. *Polym Chem* 2015;6:2312–8. <https://doi.org/10.1039/c4py01631a>.
- [70] Zucolotto Cocca LH, Pelosi A, Sciuti LF, G M, Abegão L, Kamada K, Piguel S, et al. Two-photon brightness of highly fluorescent imidazopyridine derivatives: two-photon and ultrafast transient absorption studies. *J Mol Liq* 2022;348:118379. <https://doi.org/10.1016/j.molliq.2021.118379>.
- [71] Zucolotto Cocca LH, Abegão LMG, Sciuti LF, Vabre R, de Paula Siqueira J, Kamada K, et al. Two-Photon emissive dyes based on push-pull purines derivatives: toward the development of new photoluminescence bioprobes. *J Phys Chem C* 2020;124:12617–27. <https://doi.org/10.1021/acs.jpcc.0c01859>.
- [72] Zucolotto Cocca LH, Pelosi AG, Piguel S, Mendonça CR, Boni L De. Enhancement of optical properties of new purine nucleobases containing electron-donating and -withdrawing peripheral groups. *J Photochem Photobiol B Biol* 2022;234:112524. <https://doi.org/10.1016/j.jphotobiol.2022.112524>.
- [73] Ghasemi B, Sevcik J, Nádaždy V, Végšö K, Šiffalovic P, Urbánek P, et al. Thickness dependence of electronic structure and optical properties of F8BT thin films. *Polymers* 2022;14. <https://doi.org/10.3390/polym14030641>.
- [74] Denis J-C, Ruseckas A, Hedley GJ, Matheson AB, Paterson MJ, Turnbull GA, et al. Self-trapping and excited state absorption in fluorene homo-polymer and copolymers with benzothiadiazole and tri-phenylamine. *Phys Chem Chem Phys* 2016;18:21937–48. <https://doi.org/10.1039/C6CP02059C>.
- [75] Kim JS, Lu L, Sreearunothai P, Seeley A, Yim KH, Petrozza A, et al. Optoelectronic and charge transport properties at organic-organic semiconductor interfaces: comparison between polyfluorene-based polymer blend and copolymer. *J Am Chem Soc* 2008;130:13120–31. <https://doi.org/10.1021/ja803766j>.
- [76] Urbánek P, Kuritka I. Thickness dependent structural ordering, degradation and metastability in polysilane thin films: a photoluminescence study on representative  $\sigma$ -conjugated polymers. *J Lumin* 2015;168:261–8. <https://doi.org/10.1016/j.jlumin.2015.08.022>.
- [77] Pal B, Yen WC, Yang JS, Su WF. Substituent effect on the optoelectronic properties of alternating fluorene-thiophene copolymers. *Macromolecules* 2007;40:8189–94.
- [78] Saeki A, Fukumatsu T, Seki S. Intramolecular charge carrier mobility in fluorene-thiophene copolymer films studied by microwave conductivity. *Macromolecules* 2011;44:3416–24. <https://doi.org/10.1021/ma2004844>.
- [79] Mone M, Tang S, Murto P, Abdulahi BA, Larsen C, Wang J, et al. Star-shaped diketopyrrolopyrrole-zinc porphyrin that delivers 900 nm emission in light-emitting electrochemical cells. *Chem Mater* 2019;31:9721–8. <https://doi.org/10.1021/acs.chemmater.9b03312>.
- [80] Dong W, Xue S, Lu P, Deng J, Zhao D, Gu C, et al. Functionality of peripheral side chain for enhanced performance of conjugated polymer-F8BT as an example. *J Polym Sci Part A Polym Chem* 2011;49:4549–55. <https://doi.org/10.1002/pola.24898>.
- [81] Chen N, Lu J, Wang D, Zheng C, Wu H, Zhang H, et al. A double-cable poly (fluorene-alt-thiophene) with bay-substituted perylene diimide pendants: an efficient interfacial material in bulk-heterojunction solar cells. *Macromolecules* 2018;51:80–90. <https://doi.org/10.1021/acs.macromol.7b01792>.
- [82] Murad AR, Iraqi A, Aziz SB, Abdullah SN, Brza MA. Conducting polymers for optoelectronic devices and organic solar cells: a review. *Polymers* 2020;12:1–47. <https://doi.org/10.3390/polym1212627>.
- [83] de Azevedo D, Freitas JN, Domingues RA, Faleiros MM, Atvars TDZ. Correlation between the PL and EL emissions of polyfluorene-based diodes using bilayers or polymer blends. *Synth Met* 2017;233:28–34. <https://doi.org/10.1016/j.synthmet.2017.08.015>.
- [84] Lim E, Jung BJ, Shim HK. Synthesis and characterization of a new light-emitting fluorene-thieno[3,2-b]thiophene-based conjugated copolymer. *Macromolecules* 2003;36:4288–93. <https://doi.org/10.1021/ma034168r>.
- [85] Lim E, Jung BJ, Shim HK. Improved EL efficiency of fluorene-thieno[3,2-b]thiophene-based conjugated copolymers with hole-transporting or electron-transporting units in the main chain. *J Polym Sci Part A Polym Chem* 2006;44: 243–53. <https://doi.org/10.1002/pola.21144>.



- [86] Lim E, Kim YM, Jeong-Ik L, Jung B-J, Cho NS, Lee J, et al. Relationship between the liquid crystallinity and field-effect-transistor behavior of fluorene–thiophene-based conjugated copolymers. *J Polym Sci Part A Polym Chem* 2006;44:4709–21. <https://doi.org/10.1002/pola>.
- [87] Bento DC, Barbosa CG, Roncaselli LKM, Renzi W, Duarte JL, de Almeida Olivati C, et al. Thin films of poly[(9,9-dioctylfluorene)-co-thiophene] deposited on ITO by the Langmuir–Schaefer and Langmuir–Blodgett techniques. *J Mater Sci Mater Electron* 2017;28:3875–83. <https://doi.org/10.1007/s10854-016-6000-5>.
- [88] Alves MR de A, Calado HDR, Matencio T, Donnici CL. Oligômeros e polímeros derivados do tiofeno: síntese e aplicações. *Quim Nova* 2010;33:2165–75. <https://doi.org/10.1590/s0100-40422010001000029>.
- [89] Ling QD, Li S, Kang ET, Neoh KG, Liu B, Huang W. Interface formation between the Al electrode and poly[2,7-(9,9-dihexylfluorene)-co-alt-2,5-(decylthiophene)] (PFT) investigated in situ by XPS. *Appl Surf Sci* 2002;199:74–82. [https://doi.org/10.1016/S0169-4332\(02\)00503-2](https://doi.org/10.1016/S0169-4332(02)00503-2).
- [90] Drolet N, Beaupr S, Morin J-F, Tao Y, Leclerc M. Red – green – blue light-emitting diodes containing fluorene-based copolymers. *J Opt A Pure Appl Optics* 2002;4:252–7.
- [91] Smith HL, Dull JT, Longhi E, Barlow S, Rand BP, Marder SR, et al. n-Doping of a low-electron-affinity polymer used as an electron-transport layer in organic light-emitting diodes. *Adv Funct Mater* 2020;30. <https://doi.org/10.1002/adfm.202000328>.
- [92] Cong S. Post-polymerization functionalization of conjugated polymer backbones and its applications 2019;77.
- [93] Fadavieslam MR. The effect of thickness of light emitting layer on physical properties of OLED devices. *Optik* 2019;182:452–7. <https://doi.org/10.1016/j.ijleo.2019.01.055>.
- [94] Matsushima T, Bencheikh F, Komino T, Leyden MR, Sandanayaka ASD, Qin C, et al. High performance from extraordinarily thick organic light-emitting diodes. *Nature* 2019;572:502–6. <https://doi.org/10.1038/s41586-019-1435-5>.