

Research Article

Physicochemical and Luminescent Properties of Copolymers Composed of Three Monomers: Polythiophenes Based on 3-Hexylthiophene and 3,4-Ethylenedioxythiophene

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Received 8 February 2017; Revised 4 April 2017; Accepted 9 April 2017; Published 11 May 2017

Academic Editor: Marta Fernández-García

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The chemical synthesis and physicochemical and luminescent characterizations of polymers based on 3-HT, EDOT, and 2,2'-(9,9-dioctyl-9H-fluorene-2,7-diyl) bithiophene (fluorene) or (*E*)-2-(ethyl(4-((4-nitrophenyl)diazanyl)phenyl)amino)ethyl 2-(thiophen-3-yl)acetate (TDR1) are reported. The fluorene unit was bound to the conjugate backbone, while the Disperse Red 1 (DR1) chromophore was present as a pendant group. Characterizations by ¹H NMR, FT-IR, DSC-TGA, GPC, UV-vis, cyclic voltammetry, fluorescence quantum yield, excited state lifetime, and two-photon absorption cross-section were carried out. These polymers combined the physicochemical properties of EDOT and 3-HT, such as high electron density, high charge mobility, low oxidation potential, and good processability. The optical properties of these copolymers were highly dependent on the presence of EDOT, the molecular weight, and the regioregularity rather than the presence of the third component (fluorene or TDR1). The good nonlinear absorption and luminescent properties exhibited by these copolymers were exploited to fabricate nanoparticles used as fluorescent tags for the imaging of microstructures.

1. Introduction

Conducting π -conjugated materials have been the focus of much research due to their applications in organic thin-film transistors (OTFT) [1–4], organic light-emitting diodes (OLEDs) [5–7], and photovoltaic cells [8–10], as well as for their large nonlinear optical properties and applications in biophotonics [11–13]. Their processability in organic solutions allows the production of low-cost integrated circuits

and the feasibility of using various methods, such as spin coating, ink-jet printing, and roll-to-roll printing, to fabricate large-area optoelectronic devices [14–17]. Additionally, their processability allows the use of bottom-up methods for the production of fluorescent organic nanoparticles useful in bioimaging [18].

Polythiophenes (PTs) as conducting polymers present π -conjugated backbones, good thermal and chemical stability, adequate processability, and easy functionalization [19, 20].

Moreover, the incorporation of selected substituents into the PT backbone permits the fine tuning of electronic and optical properties [21]. Likewise, copolymerization can also be utilized to combine the properties of PTs and other polymers to fine tune optical and electronics features intended for electrochromic and optoelectronic applications [22, 23].

In this context, the design of multifunctional copolymers comprising poly(3-alkylthiophenes) for potential optoelectronics and biophotonics applications is a great challenge for polymer research. 3-HT has been used to prepare regioregular copolymers by Grignard metathesis with different monomers, such as 3-alkylthiophene [24], 3-phenoxyethylthiophene [25], 1,3,4-oxadiazole [26], and 3-triphenylamine-thiophenes [27].

On the other hand, the incorporation of the EDOT monomer in π -conjugated systems represents an important strategy for developing novel materials for optoelectronic and photonic applications. These compounds can have a high degree of regioregularity, high electron affinity, high fluorescence quantum yields, and nonlinear optical properties [28, 29]. For instance, the polymerization of EDOT (PEDOT) produces favorable properties, such as a low band gap and high energy HOMO orbital, giving high stability to its conductive form. However, due to the low solubility of PEDOT, some copolymers incorporating EDOT and 3-alkylthiophene, pyrenes, or fluorenes have been synthesized. The resulting polymers/copolymers are electron rich with modifiable electronic, optical, and electrochemical properties [30]. Additionally, Lin et al. [31] developed blue-light-emitting polymers derived from EDOT en-capped dibenzothiophene and dibenzofuran, and both polymers displayed good electrochromic properties with color switching between yellow in the reduced state and purple in the oxidized state.

PTs can also be combined with other building blocks; for example, fused heterocycles represent an important class of units to achieve either a low band gap or high carrier mobility depending on the orientation of the fused ring to the polymer main chain. Fluorene is an electron-rich unit, which has been largely used as donor in D-A materials due to its interesting properties resulting from its large HOMO and LUMO energy gap [32]. Moreover, fluorene-based systems possess unique photophysical properties, such as high fluorescent quantum yields, large optical nonlinearities, large photostabilities, and excellent hole-transporting properties [33–37]. Chen et al. [38] reported the synthesis of novel alternating conjugated polymers having pyrene and thiophene/fluorene moieties in the backbone, which were successfully prepared by the Sugimoto chemical oxidative polymerization or Suzuki coupling reaction. These conjugated polymers showed efficient blue-light-emitting properties and are good candidates for pure-blue-emitting OLED applications.

Considering the above-mentioned properties and applications of PT derivatives, we present here the chemical synthesis and spectroscopic characterization of polymers derived from 3-HT, EDOT, fluorine, and TDRI. Their thermal stabilities, molecular weight distributions, and linear and nonlinear optical properties were investigated.

2. Experimental

2.1. Materials and Equipment. All reagents were purchased from Aldrich Chemical Company: 3-hexylthiophene 99%, 2,2'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bisthiophene 97%, 3,4-ethylenedioxythiophene 97%, and iron(III) chloride 97%. Anhydrous chloroform and/or nitromethane and nitrogen atmosphere were used. ^1H NMR spectra of polymers were recorded at room temperature with an INOVA 200 MHz or Varian Mercury 400 MHz spectrometers. Absorption spectra were obtained on a Spectrophotometer Genesys 10 s UV-vis with spectral window of 190 to 1100 nm. IR spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded on a Perkin Elmer Spectrum 400 spectrophotometer (ATR reflectance mode). For TGA analysis equipment, SDT Q600 V8.2 Build 100 mode was used. Average molecular weights and values of the polydispersity polymers were determined by gel permeation chromatography (GPC) on a chromatograph Alliance 2695, using polystyrene standards for calibration and two PLgel lineal columns. The cyclic voltammetry experiments were carried out using a potentiostat/galvanostat Model 2273 PARSTAT. Quantum yield and fluorescence lifetime measurements were carried out in a Spectrofluorometer FS5 from Edinburgh Instruments. Finally, the two-photon absorption (2PA) cross-section was obtained through the two-photon excited fluorescence technique [39] using rhodamine 6G molecular solution in THF at $10\ \mu\text{M}$ as comparative standard; the sample (also at $10\ \mu\text{M}$) was excited with a tunable pulsed Ti:Sapphire Laser Chameleon Ultra (Coherent), and the pulse energy and pulse width were 3 nJ and 140 fs, respectively. The induced fluorescence was recorded with a portable Spectrometer USB 4000 Ocean Optics; the 2PA cross-section was obtained from 680 nm to 1000 nm.

2.2. Oxidative Polymerization via Iron Trichloride

2.2.1. Synthesis of Poly(3-HT). A solution of FeCl_3 (19.7 g, 117.6 mmol) in 100 mL of chloroform cooled at 0°C was added dropwise to a solution of 3-hexylthiophene monomer (5.0 g, 29.4 mmol) in 80 mL of chloroform. After stirring for 24 h at room temperature for poly(3-HT)-1 or stirring for 4 h at 0°C for poly(3-HT)-2, 200 mL of methanol was added to each finished reaction. The doped polymers were added to 200 mL of a 1:1 solution of hydroxide ammonia/methanol, and the mixture was stirred for 1 h. Finally, the undoped polymers were once again filtered, washed with methanol, extracted in chloroform, evaporated, and dried. The products were obtained as a colored plastic solid, obtaining 4.25 g (87.0%) of poly(3-HT)-1 and 3.11 g (64.0%) of poly(3-HT)-2, which were soluble in chloroform.

2.2.2. Synthesis of Poly(3-HT-co-EDOT). A three-neck flask was utilized to dissolve iron chloride (11.05 g, 66.08 mmol) in dry chloroform (100 mL) and nitromethane (50 mL) under a continuous flow of nitrogen at 0°C . Then, two additional funnels were placed in the three-neck flask, and chloroform solutions (50 mL) of 3-HT (1.5 mL, 1.40 g, and 8.26 mmol) and EDOT (0.91 mL, 1.21 g, and 8.26 mmol) were added via cannula. The solutions were added dropwise to the

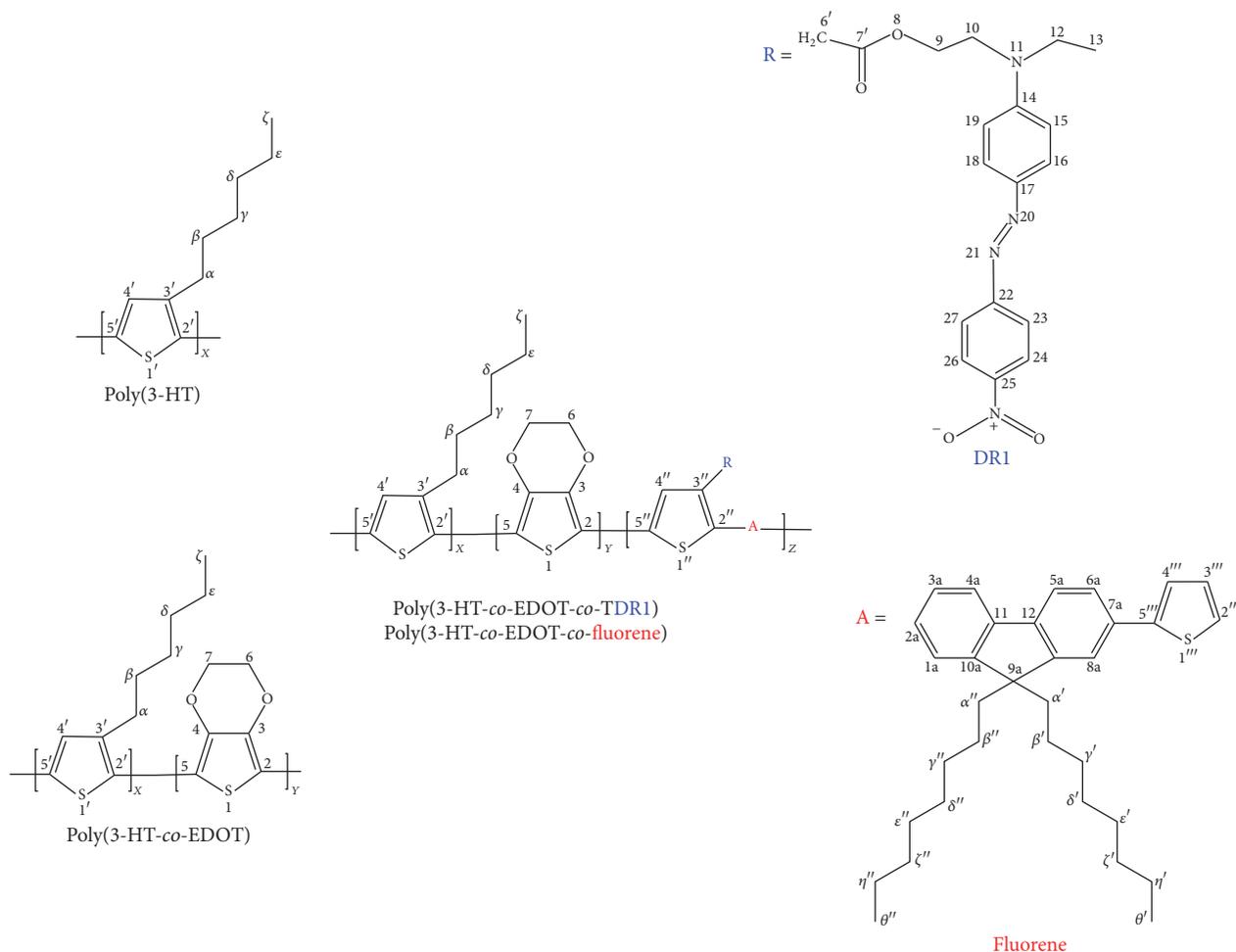


FIGURE 1: Structures of the polymers.

solution of FeCl_3 over approximately 1 h at 0°C . Subsequently, the polymerization reaction was stirred for 24 h at room temperature and finished upon the addition of 200 mL of methanol, leaving the solution to rest for one day. As a result, a dark black precipitate corresponding to the doped polymers was formed. The polymer was purified, as was described for poly(3-HT), and the soluble polymer was recovered as a black solid (0.83 g, 31.4% yield).

2.2.3. Synthesis of Polymers with Three Monomers

Poly(3-HT-co-EDOT-co-fluorene) and *Poly(3-HT-co-EDOT-co-TDR1)*. The synthesis was previously described [19]. The polymer with fluorene gave an 82.4% yield (2.72 g), while the homologous polymer with TDR1 gave a 44% yield (1.22 g). TDR1 was synthesized by our research group, as previously described in the literature [12].

2.3. Cyclic Voltammetry. A potentiostat/galvanostat with a conventional three-electrode cell was used: working electrode (platinum wire of 3 mm diameter), reference electrode (Ag+ electrode) in a solution of silver nitrate with 0.01 M

tetrabutylammonium perchlorate, 0.1 M in acetonitrile (all under anhydrous conditions), and counter electrode (platinum wire that is used to close the loop). The used solution was 3 mg of either studying polymer in 10 mL of anhydrous dichloromethane. Moreover, as the supporting electrolyte, a quaternary ammonium salt must be added, which was tetrabutylammonium perchlorate or TBAP (0.3 g of TBAP, concentration 0.1 M in dichloromethane), previously sparged with nitrogen for 45 min to eliminate further moisture.

3. Results and Discussion

To synthesize the new polymers with high molecular weights and a regioregularity of approximately 70% encompassing one to three monomers, oxidative polymerization via ferric chloride, one of the most common methods for generating poly(3-alkylthiophenes), was employed [40]. Figure 1 shows the structures of the polymers obtained.

3.1. NMR Characterization. Figure 2 shows the ^1H NMR spectra of poly(3-HT)-2, poly(3-HT-co-EDOT), and poly(3-HT-co-EDOT-co-TDR1). In general, poly(3-HT)-2 (Figure 2(a)) showed aliphatic hydrogens: $\text{H}\beta$ to $\text{H}\xi$ at 0.8–1.6 ppm and $\text{H}\alpha$

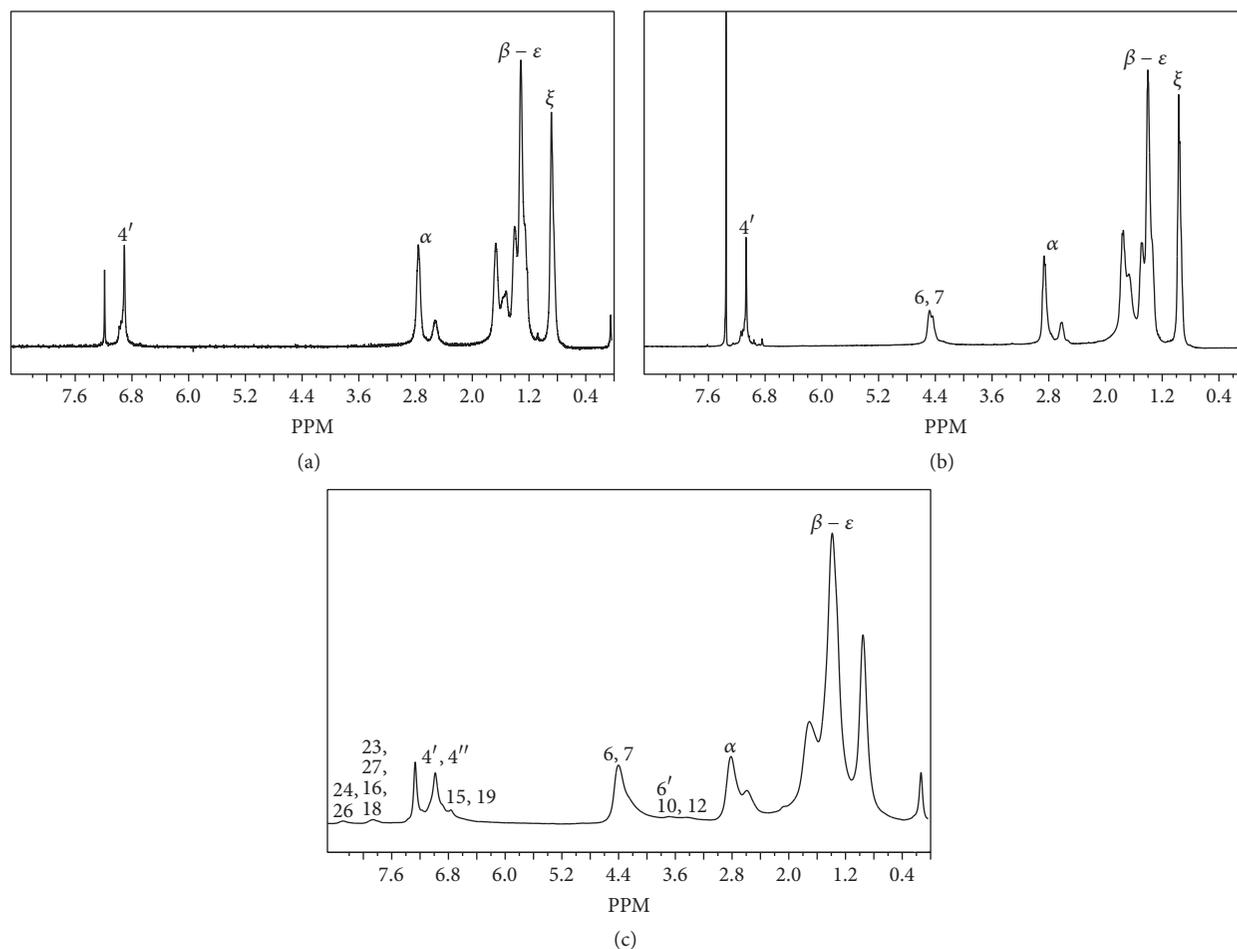


FIGURE 2: ^1H NMR spectra of (a) poly(3-HT)-2, (b) poly(3-HT-co-EDOT), and (c) poly(3-HT-co-EDOT-co-TDR1) [19] in CDCl_3 .

at 2.5 and 2.7 ppm, and $\text{H}4'$ bonded to the thiophene ring at approximately 6.9 ppm. Poly(3-HT-co-EDOT) (Figure 2(b)) presented the same signals as poly(3-HT)-2 and the signals corresponding to the methylene protons of EDOT at 4.4 ppm.

In the ^1H NMR spectrum of poly(3-HT-co-EDOT-co-TDR1), as an example of a copolymer composed of three monomers (Figure 2(c)), incorporation of the polymers components (Figures 2(a) and 2(b)) were observed. The ^1H NMR spectrum of poly(3-HT-co-EDOT-co-TDR1) (Figure 2(c)) showed weaker signals in the aromatic region, specifically in the chemical shift range of 7.8 and 8.2 ppm for the aromatic protons of the azo chromophore. This low intensity is due to the low incorporation of TDR1 in the polymer. The $x:y$ and $x:y:z$ values for each monomer in the copolymers were determined by the relative area of the peaks of the characteristic protons of each monomer. The results showed that, during the oxidative polymerization, the 3-HT and EDOT monomeric units were more reactive and incorporated easily along the polymer chain than the fluorine and TDR1 units. In consequence, the ratios of monomer (3-HT, EDOT, fluorene, or TDR1) incorporation were 38:56:6 and

55:43:2 for poly(3-HT-co-EDOT-co-fluorene) and poly(3-HT-co-EDOT-co-TDR1), respectively.

The regioregularity of the polymers was determined via ^1H NMR. It is well known that the α -methylene proton of the solubilizing alkyl chain has two different chemical shifts: one for HT and another for HH bonds [41]. In this study, the HT and HH bonds were observed at chemical shifts of 2.5 and 2.7 ppm. The polymers exhibited different regioregularity. The analysis shows that the polymers with the highest percentage of HT were poly(3-HT)-2 and poly(3-HT-co-EDOT), while poly(3-HT)-1 and copolymers based on three monomers showed lower percentages of HT. In the case of the polymers with comprising three monomers, the lower percentage of HT can be attributed to the effect of the steric hindrance of the bulky groups that intervened significantly in the regioregularity of the polymers and reactions conditions (for example, reaction time and temperature). Table 1 shows the ratios of incorporated monomers and HT and HT dyad orientations.

3.2. FT-IR Characterization. FT-IR spectroscopy provides detailed information on molecular bonding and allows for the identification of functional groups present in compounds

TABLE 1: Percentages of the incorporated monomers into the polymers and their regioregularity obtained by ^1H NMR.

Polymer	3-HT%	EDOT%	Fluorene%	TDRI%	Dyads	
					HT	HH
Poly(3-HT)-1	100				57	43
Poly(3-HT)-2	100				78	22
Poly(3-HT-co-EDOT)	78	22	—	—	80	20
Poly(3-HT-co-EDOT-co-fluorene)	38	56	6	—	68	32
Poly(3-HT-co-EDOT-co-TDRI)	55	43	—	2	70	30

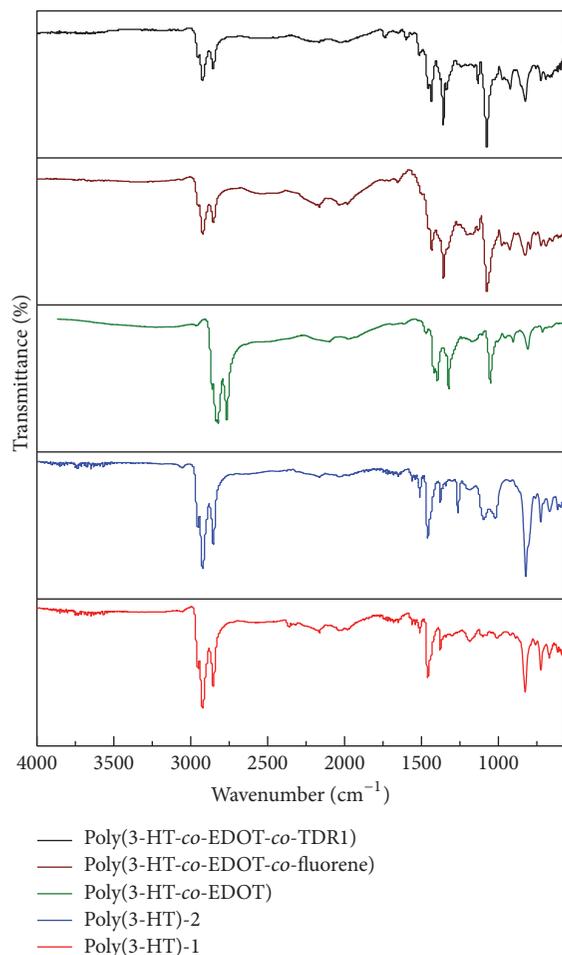


FIGURE 3: FT-IR spectra of the polymers.

through the analysis of vibrational transitions of atomic bonds [42]. FT-IR has been an excellent tool in polymer degradation studies [43–45].

To identify the functional groups of the synthesized polymers, Figure 3 presents the FT-IR spectra of the polymers. It is noteworthy to mention that the band at 784 cm^{-1} , attributed to the C-H(α) bending deformation of thiophene, is not present in these spectra, indicating the polymerization occurred through α - α coupling [46]. Additionally, the absence of a broad absorption in the range of 1390 – 1030 cm^{-1} suggests that the procedure used to remove the FeCl_3 residue

was effective [40]. As a reference, Figure 3 includes the FT-IR spectra of poly(3-HT)-1 and poly(3-HT)-2. These poly(3-hexylthiophenes) exhibit characteristic C-H stretching and C=C stretching bands that indicate the presence of the alkyl chain and the conjugated skeleton. After the inclusion of EDOT and the chromophores fluorine and DRI, the spectra changed. A new band corresponding to a C-O stretch appeared in the range of 1072 – 1078 cm^{-1} in polymers with EDOT, while the polymer with TDRI, for example, exhibited a C=O stretching band with low intensity because of the low incorporation of this third component. Table 2 summarizes the relevant FT-IR bands of the polymers.

3.3. Molecular Weight and Thermal Properties. Gel permeation chromatography (GPC) was used to determine the molecular weight distributions of the polymers using polystyrene as a standard and THF as an eluent. It is known that the molecular weight descriptors (M_n , M_w , and IPD) fluctuate depending on many factors, such as stirring speed, purification method, reaction temperature, and catalytic process [41]. In our case, the polymers had a molecular weight (M_n) between 1.2 kDa and 14.9 kDa. Table 3 summarizes the values for the distributions of molecular weights. From these results, it is evident that the copolymerization of 3-HT with EDOT tended to reduce the molecular weight; further reduction was observed after the incorporation of the chromophores (fluorene or DRI) into the copolymers. Poly(3-HT)-2 presented lower IPD and higher M_n values than poly(3-HT)-1 due to the reaction time (4 h versus 24 h) and reaction temperature (0°C versus 25°C).

The thermal stability of a conjugated polymer is very important for its potential applications [46]. The thermal properties for the synthesized polymers in our study were analyzed using TGA under a nitrogen atmosphere. Figure 4 displays the obtained thermograms. It is observed that poly(3-HT)-1 and poly(3-HT)-2, used as references for comparison purposes in this study, presented the highest thermal stabilities (at $\sim 485^\circ\text{C}$) among this set of materials. The introduction of EDOT somewhat reduced the thermal stability; that is, poly(3-HT-co-EDOT) showed a thermal stability of 463°C , while the analogs poly(3-HT-co-EDOT-co-fluorene) and poly(3-HT-co-EDOT-co-TDRI) were stable up to 413°C and 433°C , respectively. We observed a direct correlation between the decomposition temperatures of the polymers with their molecular weights (see Table 3). Poly(3-HT-co-EDOT) exhibited an 8-fold reduction of molecular weight

TABLE 2: Relevant FT-IR absorption bands (cm^{-1}) of the polymers.

Assignment (ν)	Polymers				
	Poly(3-HT)-1	Poly(3-HT)-2	Poly(3-HT- <i>co</i> -EDOT)	Poly(3-HT- <i>co</i> -EDOT- <i>co</i> -fluorene)	Poly(3-HT- <i>co</i> -EDOT- <i>co</i> -TDRI)
C-H st	2922 2853	2923 2850	2919 2846	2918 2854	2924 2855
δ_{as} (CH_3)	1456	1461	1456	1433	1455
δ_{s} (CH_3)	1376	1380	1356	1355	1357
C=C st	1509	1510	1502	1652	1597
C=O st	—	—	—	—	1730
C-O st	—	—	1074	1078	1072
C-H vibration out of plane of the thiophene ring	825	821	822	826	824
$(\text{CH}_2)_n$ rock	723	725	724	723	719

TABLE 3: Molecular weight distributions and thermal properties of the polymers.

Polymers	Mw (g/mol)	Mn (g/mol)	IPD (Mw/Mn)	T_d ($^{\circ}\text{C}$)	Weight in loss (%)
Poly(3-HT)-1	173847 \pm 0.45%	10175 \pm 1.57%	17.09 \pm 0.95%	473	65.1
Poly(3-HT)-2	79772 \pm 0.1%	14891 \pm 0.9%	5.3 \pm 1.0%	485	69.9
Poly(3-HT- <i>co</i> -EDOT)	9,837 \pm 1.5%	3,339 \pm 1.8%	2.9 \pm 3.5%	463	64.2
Poly(3-HT- <i>co</i> -EDOT- <i>co</i> -fluorene)	4108 \pm 0.7%	1238 \pm 3.8%	3.3 \pm 3.2%	413	62.9
Poly(3-HT- <i>co</i> -EDOT- <i>co</i> -TDRI)	5297 \pm 3.6%	1727 \pm 2.2%	3.0 \pm 1.6%	433	55.8

with respect to poly(3-HT)-2 and consequently a reduction in stability of 5% with respect to the same polymer. Poly(3-HT-*co*-EDOT-*co*-fluorene) and poly(3-HT-*co*-EDOT-*co*-TDRI) showed lower molecular weights (approximately 15-fold reduction) than poly(3-HT)-2; this resulted in a reduction of approximately 9–15% in the thermal stability with respect to the same polymer. We can conclude that, despite the reduction of molecular weight with the incorporation of EDOT and fluorene/DR1, the thermal stability decreased just marginally (<15%) [47].

3.4. Cyclic Voltammetry. Data obtained from cyclic voltammetry analysis to determine the HOMO and LUMO levels of the polymers are shown in Table 4. The polymers with EDOT presented a lower band gap than the poly(3-alkylthiophenes), as it has been indicated in the literature [30], which makes them good candidates for optoelectronic devices, such as organic solar cells.

3.5. Absorption and Photoluminescence. The photophysical properties of the polymers were examined using absorption-emission spectra in a dilute toluene solution (0.03 mg/mL) at room temperature. The UV-vis absorption and fluorescence spectra of these polymers are illustrated in Figure 5, while Table 5 summarizes the most important features obtained from this spectroscopy.

Poly(3-HT-*co*-EDOT) and poly(3-HT-*co*-EDOT-*co*-TDRI) showed their maximum absorbance at 457 nm, while

TABLE 4: Energy levels of the polymers.

Polymers	HOMO (eV)	LUMO (eV)	Band gap (eV)
Poly(3-HT)-1	-7.06	-4.58	2.48
Poly(3-HT)-2	-6.04	-3.15	2.89
Poly(3-HT- <i>co</i> -EDOT)	-6.41	-4.57	1.83
Poly(3-HT- <i>co</i> -EDOT- <i>co</i> -fluorene)	-6.31	-4.37	1.94
Poly(3-HT- <i>co</i> -EDOT- <i>co</i> -TDRI)	-6.54	-4.57	1.97

poly(3-HT-*co*-EDOT-*co*-fluorene) showed its maximum at 442 nm. As expected, there was a correlation between the HT content and the wavelength of the maximum absorption (λ_{max}). Higher regioregularity led to less steric hindrance between the adjacent thiophene units and consequently led to higher conjugation lengths and a larger redshift. Notably, larger regioregularities were achieved with poly(3-HT-*co*-EDOT) and poly(3-HT-*co*-EDOT-*co*-TDRI) with HT percentages of 80% and 70%, respectively, which caused a λ_{max} shift of 40 nm as compared to poly(3-HT)-1, the latter possessing the lowest regioregularity (HT percentage of 57%). Additionally, poly(3-HT-*co*-EDOT) had a higher molecular

TABLE 5: Optical properties of the polymers.

Polymers	λ_{\max}^a	λ_{em}^b	Stokes shifts (cm^{-1}) ^c	ϵ_{\max} ($\text{cm}^{-1} \text{M}^{-1}$)	Quantum yield (%)	E_{opt} (eV)
Poly(3-HT)-1	417	570	6437	347,469	21.4	2.37
Poly(3-HT)-2	440	580	5846	651,928	26.3	2.31
Poly(3-HT-co-EDOT)	457	579	4611	136,213	19.7	2.15
Poly(3-HT-co-EDOT-co-fluorene)	442	570	5081	35,815	16.5	2.15
Poly(3-HT-co-EDOT-co-TDRI)	457	574	4460	53,882	21.2	2.12

^aWavelength of absorption and ^bemission in nm. ^cStokes shifts in cm^{-1} .

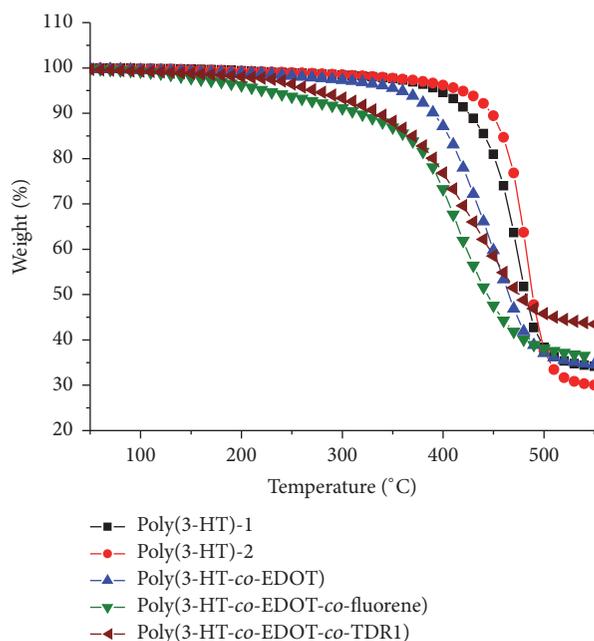


FIGURE 4: Thermograms for the polymers.

weight than the copolymers with three components, which was reflected as an improvement in ϵ_{\max} (Table 5). This table also includes the optical band gap (E_{opt}) of each polymer calculated from a linear extrapolation of the absorption edge at the axis of zero absorption. From the absorption spectra, the introduction of EDOT reduced E_{opt} , which agrees with the tendency observed for the electronic band gap obtained by cyclic voltammetry. Regarding the photoluminescence properties, the emission spectra for the copolymers under UV excitation (365 nm) were unaffected by the introduction of EDOT and the chromophores, showing emission peaks (λ_{em}) at approximately 575 nm and small shoulders at 640 nm, as seen in Figure 5(b). The emission spectra were dominated by the emission of the 3-HT monomer. Only the spectrum of poly(3-HT-co-EDOT-co-fluorene) differed slightly from those of the rest of polymers, showing a blue-greenish emission in the range from 475 to 525 nm. Hypothetically, this emission at the edge of the spectrum could result from the conjugated fluorene unit, which typically exhibits very efficient quantum yields of fluorescence, but here, this emission was just partially observed due to the relatively low concentration achieved for such unit in the copolymer. The

emission of the TDRI monomer (approximately 550 nm) in poly(3-HT-co-EDOT-co-TDRI) was not discriminated from the emission of 3-HT mainly due to the overlap of both spectra and the low concentration of the TDRI monomer. The fluorescence quantum yields of the poly(3-HT-co-EDOT), poly(3-HT-co-EDOT-co-fluorene), and poly(3-HT-co-EDOT-co-TDRI) copolymers at low concentrations (10 μM) were determined using an integrating sphere method and resulted in values of 19.7, 16.5, and 21.2%, which were very similar to that of the poly(3-HT)-1 polymer. Likewise, the fluorescence lifetime decay was measured by a time-correlated single photon counting (TCSPC) technique. In this case, the fluorescence of each compound was represented by a monoexponential decay (data not shown) with a decay time constant of approximately 0.85 ns. According to these results, in these copolymers, the regioregularity (68–80% HT dyads), molecular weight ($M_n = 1.2$ to 3.3 KDa), and percentage of 3-HT incorporation (38–78%) primarily determined the absorption and emission properties more than the presence of additional groups; for example, poly(3-HT-co-EDOT-co-fluorene) had the lowest percentage of HT dyads (68%), molecular weight ($M_n = 1.2$ KDa, IPD = 3.3), and percentage of 3-HT (38%) among the copolymers, and thus, it had the lowest extinction coefficient ϵ_{\max} and quantum yield.

3.6. 2PA Cross-Section. The nonlinear absorption of conjugated polymers at infrared wavelengths is one of the most useful optical properties for a variety of applications. Polymers that exhibit fluorescence excited by the nonlinear absorption of two photons (2PA) have applications in bioimaging. The quantification of 2PA is expressed by the molecular cross-section ($\sigma_{2\text{PA}}$) in Göppert-Mayer units (1 GM = $10^{-50} \text{cm}^4 \text{s photons}^{-1} \text{molecules}^{-1}$). Figure 6 presents the values of $\sigma_{2\text{PA}}$ obtained for the copolymers at different infrared wavelengths. The dispersion of $\sigma_{2\text{PA}}$ values represents the nonlinear absorption spectra. These nonlinear absorption spectra are very similar for all the copolymers, displaying a peak of approximately 500 GM at 740 nm for poly(3-HT-co-EDOT) and poly(3-HT-co-EDOT-co-TDRI), while, for poly(3-HT-co-EDOT-co-fluorene), the peak is 420 GM at 720 nm.

All three copolymers exhibited good fluorescence induced by 2PA making them suitable candidates as fluorescent tags in imaging applications for microstructures. To demonstrate this assumption, we prepared nanoparticles of the copolymers under study and used them as fluorescent tags in microstructures. The nanoparticles were fabricated

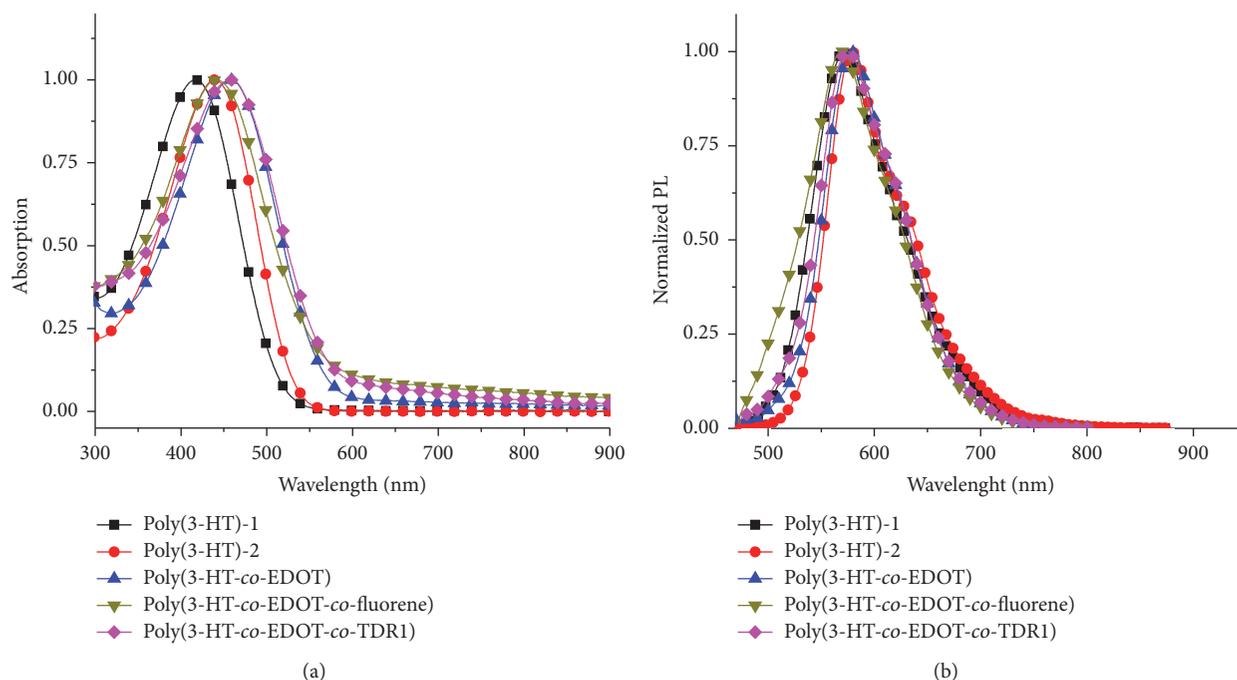


FIGURE 5: (a) Absorption and (b) emission spectra of the polymers. The emission spectra were obtained under UV excitation at 365 nm.

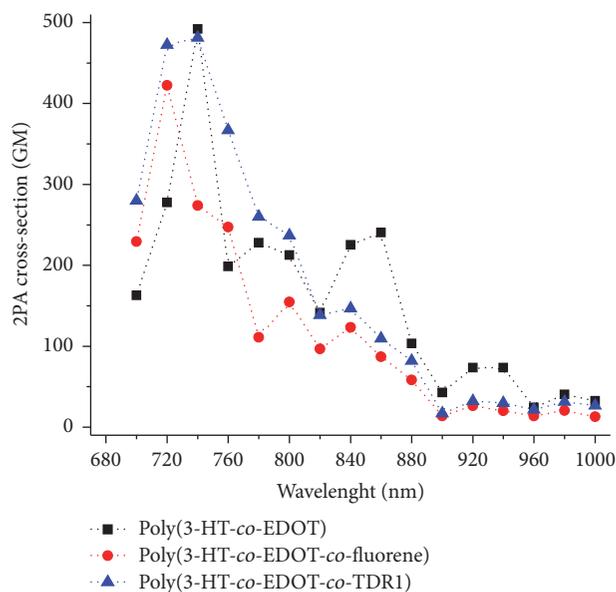


FIGURE 6: 2PA cross-section of the polymers. The dotted lines are guides for the eyes.

using a reprecipitation method. Briefly, a small volume of copolymer solution (<0.5 mL) was injected quickly (using a microsyringe) into a larger volume of water (>8 mL) under sonication, and the copolymer underwent reprecipitation in the form of nanoparticles. The size of the nanoparticles measured by dynamic light scattering (DLS) varied in the range 120–180 nm according to the utilized volumes of solution and water. A suspension of nanoparticles was mixed

with a solution of polyvinyl alcohol (PVA). Based on the host (PVA)-guest (nanoparticles) approach, thin films (thicknesses of $\sim 1 \mu\text{m}$) of PVA doped with copolymer nanoparticles were deposited on glass substrates by spin coating. Then, using a laser ablation stage (Laser mFAB, Newport) a microstructure was patterned on each film. Figure 7(a) shows the typical patterns observed by a standard optical microscope consisting of lines of $150 \mu\text{m}$ in length separated by $50 \mu\text{m}$. Since these microstructures are made of polymer nanoparticles with luminescent properties and 2PA activity, they can be visualized using fluorescence microscopy with infrared laser excitation. As an example, Figure 7(b) presents the micrograph from a microstructured PVA film doped with nanoparticles of poly(3-HT-co-EDOT); this image was obtained using a multiphoton microscope (LSM 710 NLO, Zeiss) with excitation at 750 nm. As we can see in Figures 7(a) and 7(b), the patterns are regular and well resolved using both the standard and fluorescence microscope, indicating that the nanoparticles disperse homogeneously in the film without significant aggregation. These micrographs demonstrate the feasibility of using nanoparticles of copolymers for biophotonic applications; that is, nanoparticles made of copolymers can be used as exogenous fluorescent tags to be internalized into cellular lines or biological tissues to study their structures or dynamics using a fluorescence microscope.

4. Conclusions

The chemical syntheses of polymers derived from 3-HT and EDOT through oxidative polymerization were described. ^1H NMR was used to determine the percentages of each monomer unit and the percentages of the HT dyads. The

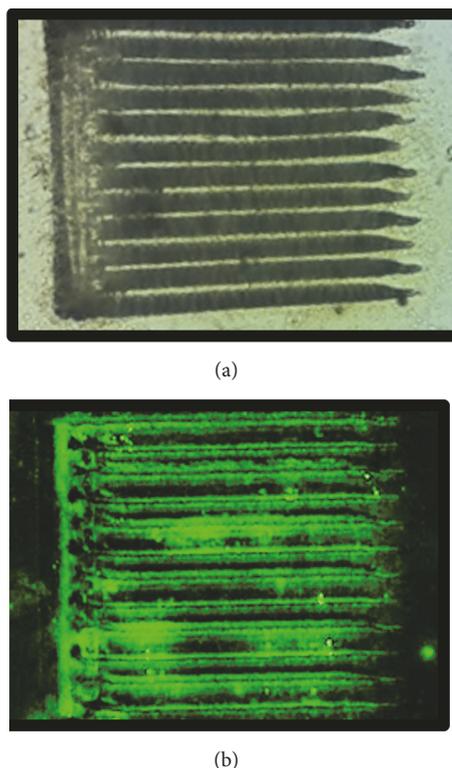


FIGURE 7: PVA film doped with nanoparticles made of the poly(3-HT-co-EDOT) copolymer. Images of the film obtained with (a) standard optical microscopy and (b) fluorescence microscopy with infrared excitation at 750 nm. The micropattern on the PVA film consists of lines of 150 μm in length separated by 50 μm .

incorporation of fluorene or TDR1 was less than 10%, while the regioregularities were between 70 and 80% for the polymers with EDOT. TGA-DSC analysis indicated that the polymers are stable with high decomposition temperatures ($>400^\circ\text{C}$), which were lower for the polymers with three components. Furthermore, the polymers with EDOT presented lower band gaps than the analogous poly(3-hexylthiophenes). Due to the low percentage of the Z fragment (fluorene bound to the conjugate backbone and DRI as a pendant group), its presence did not significantly affect the optical properties. Thus, the molecular weight, regioregularity, and percentage of 3-HT incorporation primarily determined the optical properties of these copolymers based on three monomers. The good nonlinear properties of nanoparticles made with these copolymers were exploited to demonstrate their use as fluorescent tags for the two-photon imaging of microstructures.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

The authors are grateful for the financial support from CONACyT projects (CB2015-257543-Q and 215708) and also

acknowledge the recognition of CIICAp-IICBA (UAEM), CIQ-IICBA (UAEM), and the Laboratory of Ultrafast Optics at CIO for the use of facilities and the support services provided in this research.

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