

Research Article

SYNTHESIS AND OPTICAL PROPERTIES OF NOVEL CONJUGATED POLYMER BASED ON THIALCALIX[3]TRIAZINE AND 3-HEXYLTHIOPHENE

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ABSTRACT

In this study, we synthesized the novel conjugated polymers based on thiacalix[3]triazine and 3-hexylthiophene via C-H direct arylation polymerization. The chemical structure of obtained conjugated polymers has a donor – acceptor moieties including thiacalix[3]triazine as acceptor units due to electron withdrawing properties of triazine and donor moieties such as 3-hexylthiophene. The structure of the resulted polymer was characterized via FTIR and ¹H NMR spectrum. In addition, the molecular weight of the polymer was determined by GPC analysis. The optical properties of the polymer were investigated via UV-Vis and PL spectrometer. The novel conjugated polymers have been expected to have a narrow band-gap and redshift absorption and could be applied for organic solar cells (OSCs)

Keywords: C-H direct arylation polymerization; conjugated polymers; donor – acceptor polymers; thiacalix[3]triazine

1. Introduction

Organic solar cells have recently received great consideration due to their advantages of low cost, lightweight, processability, and high mechanical flexibility. In particular, conjugated molecules is a matter of high current interest as active materials for organic electronic devices such as organic field-effect transistors (OFETs), polymeric light emitting diodes (PLEDs), electrochromic displays, or organic solar cells (OSCs) (Cheng et.al., 2009; Arias et. al., 2010; Jørgensen et. al., 2012; Zhou et. al., 2012; Li et. al., 2012; Su et. al., 2012; Janssen et. al., 2013). Among the building units for synthesis of conjugated polymers, 3-hexylthiophene and its derivatives have been extensively used in conjugated polymer for hole-transporting polymer layer in photo-electronic application especially for synthesis of regular poly(3-hexylthiophene) for organic solar cells. Regio regular poly(3-

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hexylthiophene) (rr-P3HT) has been widely studied because of the excellent performance in terms of solubility, chemical stability, charge mobility, and commercial availability (Ludwigs et. al., 2014; Kim et. al., 2011). Examples of the synthesis of star P3HTs by different synthetic pathways have been reported by several groups. In the present, the donor – acceptor conjugated polymers have emerged in the past ten years as potential materials for efficient organic solar cells that reached more than 12% of power conversion efficiency in polymeric solar cells. The crucial factor to achieve those characteristics is conjugated polymer with a donor-acceptor (D-A) structure, which possess the narrow bandgap, charge carrier mobility, energy levels, and absorption range. Many of the D-A low bandgap conjugated polymers consist of an electron acceptor and an electron donor moiety (Choi et. al., 2015; Zhou et. al., 2011; Geng et. al., 2014). For synthesis, to avoid the disadvantages of traditional polymerization reactions, the direct (hetero)arylation polymerization emerges to be a prospective strategy due to its various benefits such as simplified and shortened procedure and the prevention of using organometallic compounds and acquaintance of a lower environmental impact. These advantages allow C-H direct arylation to be widely used for synthesis of D-A conjugated polymers (Liu et. al., 2018; Yu et. al., 2017; Nitti et. al., 2017). On the other hand, Heteracalixarenes have attracted considerable attention in supramolecular chemistry in recent years because of their self-assembling ability (Chen et. al., 2016; Dariee et. al., 2017). Thiacalix[3]triazine is a subclass that has been proven to be suitable as macrocyclic scaffolds depending on anion binding moieties (Lhoták et. al., 2004; Morohashi et. al., 2006). Thiacalix[3]triazine is constructed from 1,3,5-triazines, enforced as electron-deficient host for halide ion binding through anion- π interactions. Thiacalix[3]triazine can be prepared by condensation of a dichloro-1,3,5-triazine with sulfide ion. The synthesis of thiacalix[3]triazines with peripheral phenol or tert-butyl substituents from the reaction of corresponding 2,4-dichloro-1,3,5-triazine with NaSH or alternatively Na₂S has been reported. Thiacalix[3]triazine has been shown to interact with non-protic and less-acidic protic anions via the anion association mechanism, and with more-acidic protic anions following the protonation mechanism (Van et. al., 2013).

In this study, we synthesized the new conjugated polymer based on thiacalix[3]triazine and 3-hexylthiophene via C-H direct arylation polymerization where the Palladium(II) acetate and tricyclohexylphosphine tetrafluoroborate were used as a catalytic system. The obtained conjugated polymer was characterized by ¹H NMR, FTIR, and GPC to determine the chemical structure as well as the molecular weight of polymers. The optical properties of polymer were then investigated by UV-Vis and PL to find its bandgap and its photoluminescence characteristic.

2. Experiment

2.1. Materials

The chemicals used in this research have been listed as table below:

Number	Chemical name	Formula	Purity
01	Cyanuric chloride	C ₃ Cl ₃ N ₃	99.8%
02	Phenol	C ₆ H ₆ O	99.8%
03	Sodium hydrosulfide	NaSH	99%
04	Potassium acetate	CH ₃ CO ₂ K	99%
05	Sodium carbonate	Na ₂ CO ₃	99%
06	Magnesium sulfate	MgSO ₄	98%
07	3-Hexylthiophene	C ₁₀ H ₁₆ S	98%
08	N-bromosuccinimide	C ₄ H ₄ BrNO ₂	99.5%
09	Palladium(II) acetate	Pd(OAc) ₂	99%
10	4'-bromoacetophenone	C ₈ H ₇ BrO	98%
11	tricyclohexylphosphine tetrafluoroborate	Pcy ₃ .HBF ₄ ,	97%
12	Iodobenzene diacetate	C ₁₀ H ₁₁ IO ₄	98%
13	Chloroform	CHCl ₃	99.5%
14	Toluene	C ₇ H ₈	99.5%
15	Tetrahydrofuran	C ₄ H ₈ O	99%
16	Dichloromethane	CH ₂ Cl ₂	99.8%
17	n-heptane	C ₇ H ₁₆	99%
18	Methanol	CH ₃ OH	99.8%
19	Ethyl acetate	C ₄ H ₈ O ₂	99%
20	Diethyl ether	(C ₂ H ₅) ₂ O	99%

2.2. Characterization

Proton nuclear magnetic spectra were recorded in deuterated chloroform solvent (CDCl₃) with TMS as an internal reference, on a Bruker Avance 300 at 300 MHz. Fourier-transform infrared spectroscopy spectra were collected as the average of 524 scans with resolution of 4 cm⁻¹ on a FT-IR Tensor 27 spectrometer. Thin layer chromatography plates were purchased from Sigma-Aldrich.

Absorption properties of polymer in solution and solid state film were recorded by UV-vis performed on Ocean array spectrometer over a wavelength range of 300–900 nm. The concentration of polymer in chloroform was about 10⁻⁶ M and polymer thin films were prepared from solution and spin-coated onto glass substrates and dried in a vacuum for two hours. Fluorescence spectra were measured on an ocean PL spectrometer.

Gel permeation chromatography (GPC) measurements were performed on a Polymer PL-GPC 50 gel permeation chromatography system equipped with a RI detector, with tetrahydrofuran as the eluent (flow rate: 1.0 ml/min). Molecular weight and molecular weight distribution were calculated regarding polystyrene standards.

2.3. Synthesis of 2,4-Dichloro-6-phenoxy-1,3,5-triazine compound

Cyanuric chloride (7) (1.840 g, 10 mmol) was dissolved in acetone (100 mL) and cooled to 0°C. In a separate flask, phenol (0.94 g, 10 mmol) was reacted with NaOH (0.400 g, 10 mmol) in water (100 mL) to form a clear aqueous solution. Then, the aqueous solution was added dropwise to the cyanuric chloride solution. After stirring at 0°C for 8 h, the mixture was poured into water (100 mL) to form a white precipitate. The white precipitate was filtered and washed with water and ethanol. The product was purified by recrystallization with *n*-hexane to give a white solid. Yield: 80%. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.43-7.36 (m, 4H), 7.28 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.17–7.11 (m, 4H).

2.4. Synthesis of 4,6,10,12,16,18,19,20,21-nonaaza-5,11,17-triphenoxy-2,8,14-trithiacalix [3]arene (thiacalix[3]triazine)

2,4-dichloro-6-phenoxy-1,3,5-triazine (2 g, 8.26 mmol) was dissolved in dry THF and the solution was purged with nitrogen for 10 min. NaSH (0.86 g, 15.30 mmol) was added to the solution and the reaction was carried out at 60 °C for 72 h. After completion of the reaction, the solution was dissolved in a mixture of dichloromethane and distilled water. The organic fraction was then washed with water, dried with K₂CO₃, filtered and solvent evaporated to dryness. The crude products were purified over a silica column using the mixture of the solvent of *n*-heptane/ethyl acetate as eluent (volume/volume: 3/1) to obtain a light yellow powder as the pure product. The yield of the reaction was estimated at about 18%.

2.5. Synthesis of conjugated polymer P1 based on thiacalix[3]triazine and 3-hexylthiophene

Thiacalix[3]triazine (0.34 mmol) and 2,5 dibromo-3-hexylthiophene (0.23 mg) were dissolved in 10 mL DMAc in a 100 mL flask under nitrogen. Then, Pd(OAc)₂ (3.80 mg, 0.05 mmol), PCy₃.HBF₄ (12.46 mg, 0.10 mmol), PivOH (34.57 mg, 1.00 mmol) and K₂CO₃ (140.35 mg, 3.00 mmol) were added into the flask, the solution was heated at 110°C and stirred for 24h. Then, the mixture was cooled down to room temperature and the polymer was precipitated by addition of 50 ml of methanol and filtered through a Soxhlet thimble, which was then subjected to Soxhlet extraction with methanol, *n*-hexane, and chloroform. Next, the resulting solution from the chloroform fraction was precipitated in 50 ml of methanol. The polymer was recovered as a greyish solid sample by filtration and dried under vacuum at 50°C for 24h to obtain the final product P1 (68 mg, yield 56%).

¹H NMR (500 MHz, CDCl₃), δ (ppm): 6.5-8.5 (m, 10H), 3.49 (s, 1H), 0.88-1.63 (m, 15H). FT-IR (cm⁻¹): 3045, 2935, 1585, 1491, 1274, 1087, 1014, 812, 720, 621. GPC (Gel permeation chromatography): M_n (The number average molecular weight of polymers) = 8.000 g/mol. Đ (M_w/M_n) (polydispersity index of polymer) = 2.27.

3. Results and discussion

The monomer thiacalix[3]triazine has been characterized via ^1H NMR. Figure 1a exhibited the ^1H NMR of the monomer. The peaks from 7.15 to 7.40 ppm in Figure 1b are attributed to aromatic protons of the thiacalix[3]triazine. In addition, the ^{13}C NMR of the monomer has also been analyzed to confirm the chemical structure. These results suggested that the thiacalix[3]triazine has been synthesized successfully.

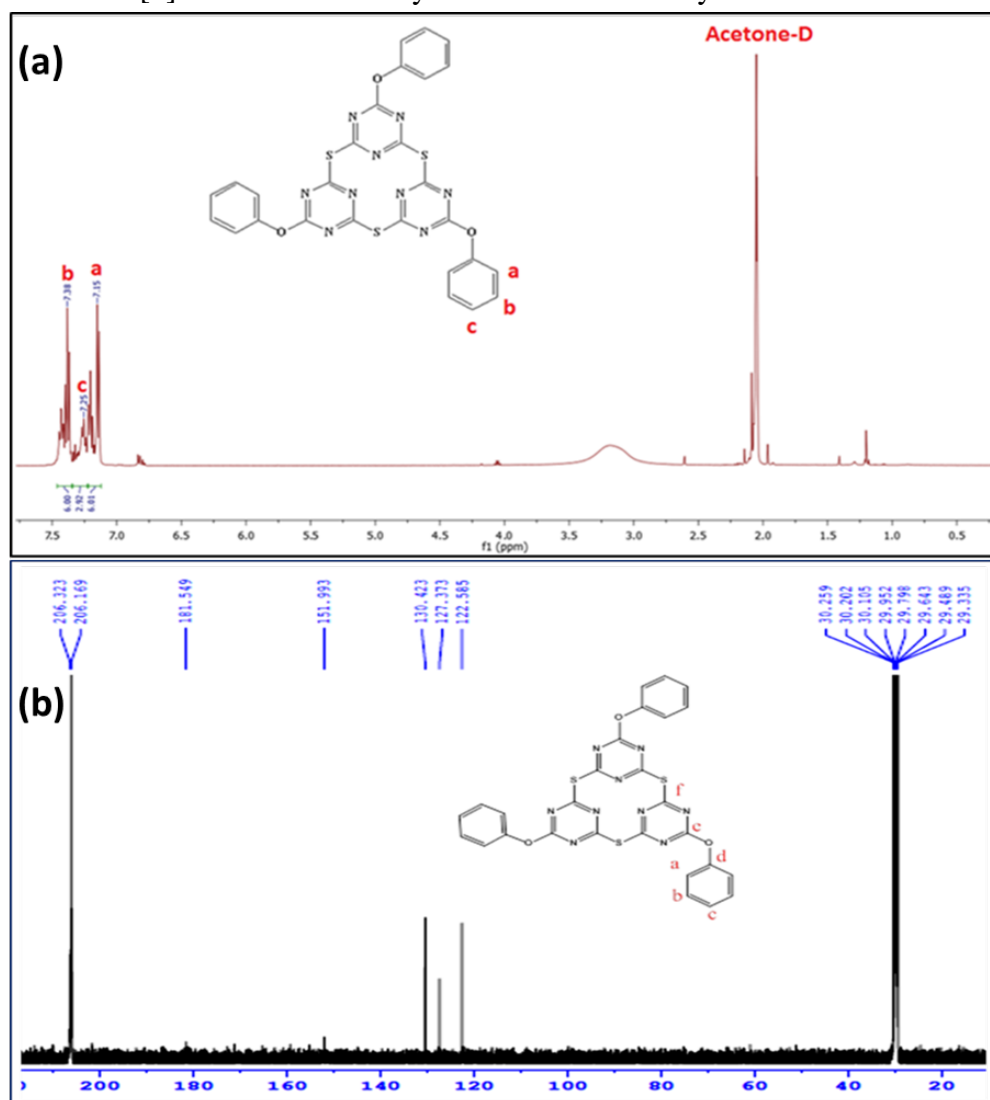
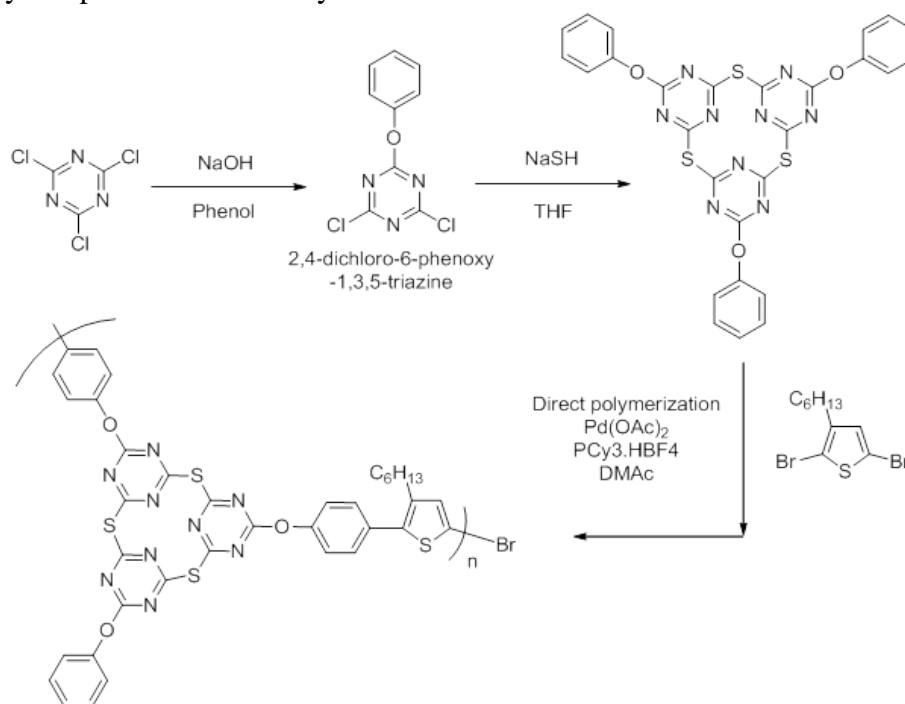


Figure 1. The ^1H NMR spectrum of 2,4-Dichloro-6-phenoxy-1,3,5-triazine monomer (a) and ^{13}C NMR of 2,4-Dichloro-6-phenoxy-1,3,5-triazine monomer (b).

The polymer P1 was synthesized via direct arylation polycondensation which was carried out by the catalyst system of $\text{Pd}(\text{OAc})_2$ and $\text{PCy}_3\cdot\text{HBF}_4$ as ligand. The reaction was performed in DMAc solvent at 100 °C. In the case of P1, at the early stage of the reaction, the color of mixture was light yellow then changed to green after 2h and turned to dark green after 24h. After the reaction finished, polymer P1 was dissolved in CHCl_3 and filtrated via

a celite layer to eliminate the Pd catalyst, and then the polymers were obtained by precipitation in cold methanol. The yields of polymerizations were obtained about 56%. Scheme 1 presented the synthesis of monomer and polymers based on thiacaliax[3]triazine and 3-hexylthiophene via direct arylation.



Scheme 1. Synthesis of P1 based on thiacaliax[3]triazine and 3-hexylthiophene

The polymer P1 was characterized via gel permeation chromatography (GPC) to determine the relative number molecular weights of polymers. P1 exhibited the average molecular weight of 8000 g/mol with polydispersity index (\bar{M}_w/\bar{M}_n) of 2.27. Although the time reaction has been extended more than 24h, the molecular weight of polymer remains at 8.000 g/mol. This result can be explained that the polymer has a rigid structure resulting from the decrease of polymerization degree. The structures of P1 was characterized by FTIR and ^1H NMR spectroscopies. The FTIR spectra of P1 displayed the bands between 2850 and 3062 cm^{-1} due to C=C stretching of aromatic structure and C-H deformation vibrations. The peaks at 1585 cm^{-1} and 1491/1473 cm^{-1} are ascribed to the aromatic C=C stretching and aromatic C-H deformation vibrations, respectively. In addition, the peaks at 1317 cm^{-1} and 1274 cm^{-1} are ascribed to the C-N stretching of triphenylamine units. The bands at 1087 cm^{-1} and 1150 cm^{-1} indicates the presence of C-O stretching vibration. The bands between 621 cm^{-1} and 752 cm^{-1} are ascribed to the long chains methyl rocking vibration. Figure 2 exhibited the FTIR of the conjugated polymer P1.

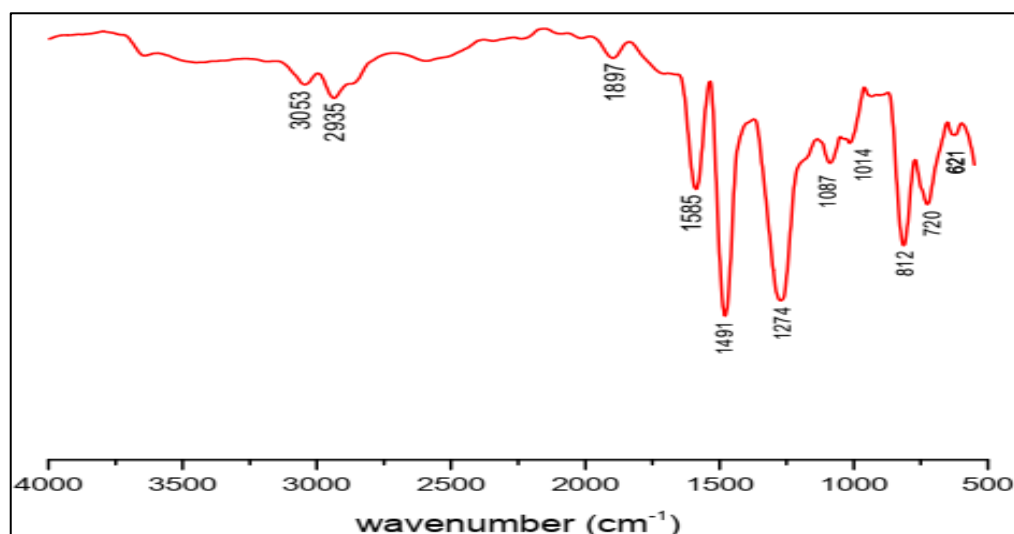


Figure 2. FTIR of polymer P1

In the ¹H NMR spectrum of polymer P1, the peaks from 8.0 to 6.5 ppm are corresponding to aromatic rings in the polymer structure. The peak at 3.49 ppm and the peaks from 2.0 to 0.5 ppm corresponded to the alkyl side chain of 3-heptylthiophene units. These results indicated that polymers were successfully synthesized via direct heteroarylation polymerization.

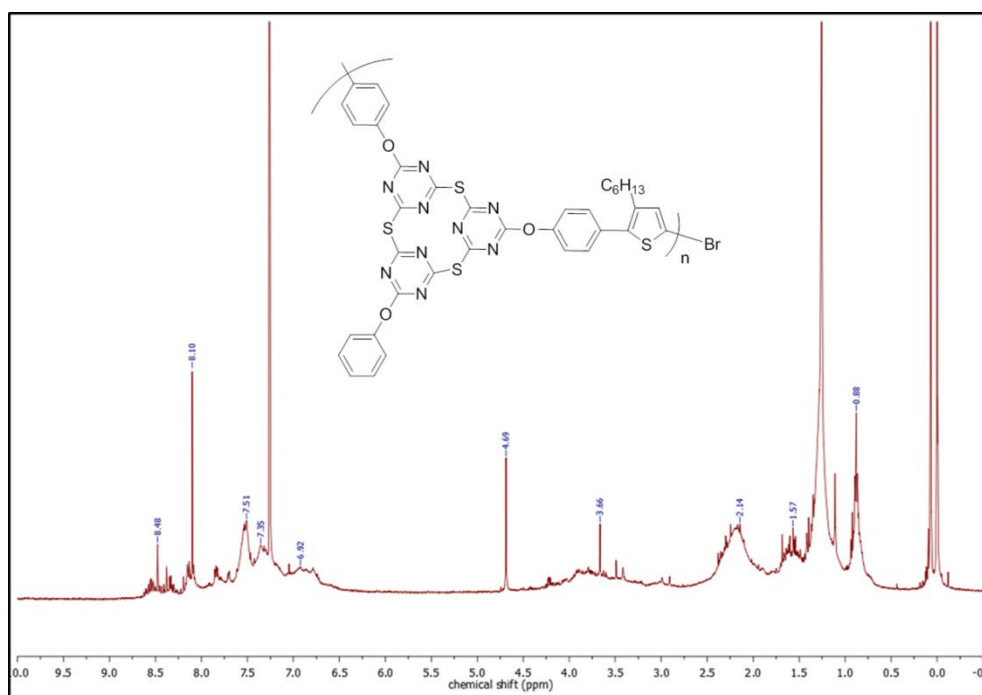


Figure 3. ¹H NMR of polymer P1

To investigate the optical properties of polymer P1, UV-vis spectroscopy has been applied for the polymer that dissolved in THF and a solid state film. Figure 4 showed the normalized UV-vis absorption spectra. Polymer P1 in solution exhibited an absorption peak

at 425 nm in solvent, while polymer P1 also showed a slightly red shifted absorption with the maximum at 430 nm in solid state film. The absorption of the polymer film was not redshift comparing to the absorption in solution. This result can be explained that the structure of polymers was bulky, which hindered the aggregation of polymer chains. It is clear that the maximum absorptions of polymer P1 in both solution and solid state film were not much different. This can be explained that the structure of P1 has the branched structure leading to the less aggregation of polymer chains. As a result, the polymer was less absorbed at the redshift area. Based on UV-vis spectroscopy, the optical band gaps (E_g^{opt}) of 2.50 has been determined for polymer P1 due to the absorbance onset (λ_{onset}) of the polymer at 500 nm according to the equation: Energy (E) = Planks Constant (h) x Speed of Light (C) / Wavelength (λ_{onset})

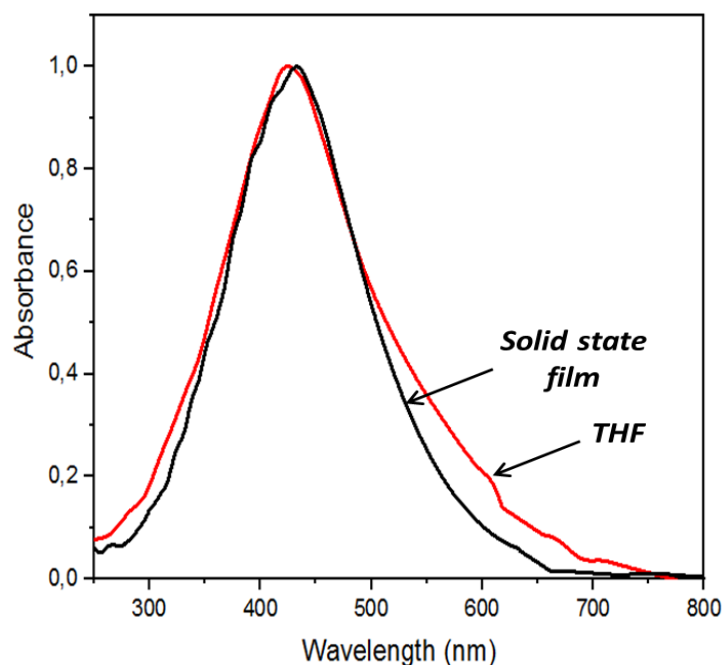


Figure 4. The UV-Vis spectroscopy of polymer P1

In addition, the polymer P1 was investigated for the photoluminescence properties via the photoluminescent spectra (PL) of this polymer in a solution of THF and chlorobenzene solvents with the wavelength excitation at 470 nm. In chlorobenzene, the polymer P1 displayed an emission peak at 538 nm, whereas in THF (10^{-3}), P1 exhibited a peak at 550 nm (Fig. 5).

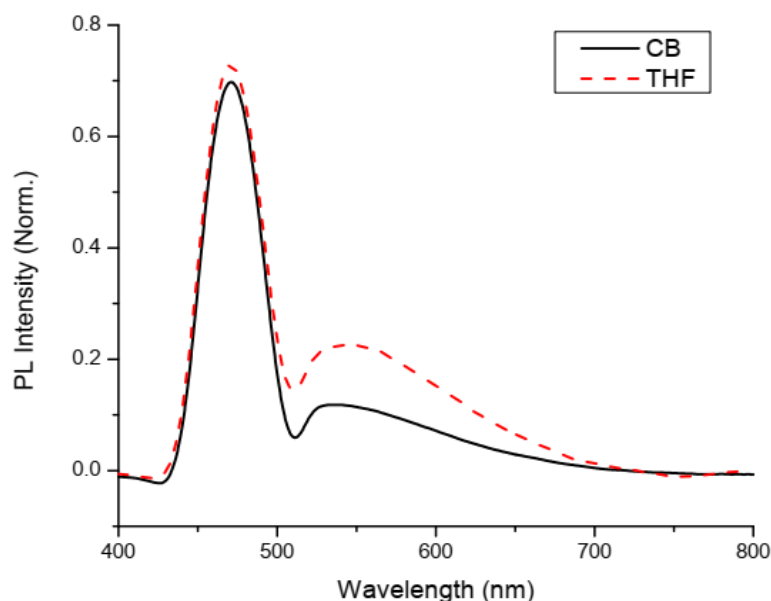


Figure 5. PL spectra of polymers P1 in chlorobenzene and in THF

4. Conclusion

In conclusion, the donor-acceptor conjugated polymer based on thiocalix[3]triazine and 3-hexylthiophene has been synthesized using a direct arylation polymerization in the presence of the Pd catalyst system. The obtained conjugated polymer P1 showed the number average molecular weight of 8000 g/mol with polydispersity index (\bar{M}_w/\bar{M}_n) of 2.27. The polymer P1 exhibited the optical band gap of 2.5 eV that is suitable as a semiconducting layer in organic solar cell devices.

❖ **Conflict of Interest:** Authors have no conflict of interest to declare.

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TỔNG HỢP VÀ ĐÁNH GIÁ TÍNH CHẤT QUANG CỦA POLYMER CẤU TRÚC LIÊN HỢP MỚI TRÊN CƠ SỞ THIACALIX[3]TRIAZINE VÀ 3-HEXYLTHIOPHENE

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TÓM TẮT

Trong nghiên cứu này, chúng tôi đã tổng hợp polymer cấu trúc liên hợp mới dựa trên đơn vị monomer thiocalix[3]triazine và 3-hexylthiophene qua phản ứng polymer hóa trực tiếp ghép đôi C-H. Cấu trúc polymer liên hợp được tổng hợp có cấu dạng cho – nhận điện tử trong đó đơn vị thiocalix[3]triazine đóng vai trò như là chất nhận điện tử nhờ vào tính chất hút điện tử của nhóm vòng triazine và 3-hexylthiophene đóng vai trò là chất cho điện tử. Cấu trúc hóa học của polymer được phân tích qua phương pháp phân tích phổ hồng ngoại FTIR và phổ cộng hưởng từ hạt nhân. Trọng lượng phân tử của polymers được xác định qua phân tích sắc ký gel GPC. Tính chất quang học của polymer được khảo sát bằng phổ UV-vis và PL. Polymer cấu trúc liên hợp mới này thể hiện độ hẹp vùng cấm, khả năng hấp thụ vùng ánh sáng nhìn thấy và khả năng ứng dụng trong việc chế tạo pin mặt trời nền hữu cơ (OSCs).

Từ khóa: phản ứng polymer hóa trực tiếp ghép đôi C-H; Polymer cấu trúc liên hợp; polymer cấu dạng cho nhận điện tử; thiocalix[3]triazine