



From monomer to polymer: Controlled synthesis and comprehensive analysis of poly(*p*-phenylene vinylene) via ROMP

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ABSTRACT

This study focuses on synthesis and evaluation of [2.2] paracyclophane-1,9-diene to produce a soluble poly(*p*-phenylenevinylene) (PPV) derivative homopolymer using ring-opening metathesis polymerization (ROMP). The resulting homopolymer displayed a narrow polydispersity index (PDI) of 1.22, indicating precise control over polymerization. The PPV derivative exhibited excellent solubility in various organic solvents. Photophysical properties, including optical absorption and fluorescence emission spectra, were investigated to evaluate utilization in optoelectronic devices. Optical band gaps ranged from 2.21 to 2.25 eV for thin films and 2.07 to 2.19 eV for solutions, while the electrochemical band gap, determined by cyclic voltammetry, was 2.37 eV. These materials demonstrated promising fluorescence activity in various solvents and thin films, suggesting potential applications in organic light-emitting diodes (OLEDs) and related optoelectronic devices.

1. Introduction

Conjugated polymers (CPs) are a class of organic materials featuring an alternating carbon backbone that facilitates electron transfer to develop new technologies in order to utilize renewable energy sources [1–4]. Notable examples include polyacetylene (PAC) [5], poly-*para*-phenylene (PPP) [6], polythiophene (PTh) [7], polypyrrole (PPy) [8], polyaniline (PA) [9], and polyfluorene (PF) [10]. These materials are gaining prominence due to their impressive attributes such as high fluorescence efficiency, prolonged stability, color adjustability, robust processability, straightforward synthesis, mechanical flexibility, and cost-effectiveness. Among the widely studied conjugated polymers is poly(*p*-phenylene vinylene) (PPV), a semiconducting polymer comprising alternating *para*-phenylene and vinylene units [11–18]. PPV finds applications in diverse fields, including organic light-emitting diodes (OLEDs) [18–22], organic field-effect transistors (OFETs) [23], organic photovoltaic cells (OPVs) [24], bioimaging [25], drug delivery systems [26], and biological and chemical sensors [27]. Various synthesis techniques [28,29], as outlined by Suzuki [30], Stille [31], Kumada [22], Negishi [32], Ziegler–Natta [27], Wessling [14],

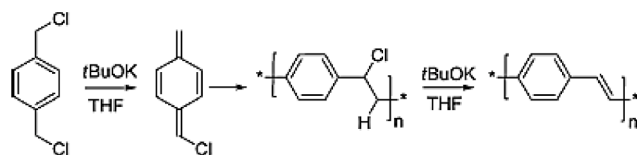
Sonogashira [33], and metathesis [34], can be employed for PPV preparation.

One method that was employed to realize soluble PPVs was the polymerization of symmetrical α,α' -dichloro *p*-xylylene as a monomer in the presence of a significant excess of potassium tert-butoxide (KtBuO) [Scheme 1], which was authorized by Gilch and Wheelwright in 1966 [35]. However, the main drawback with such an approach is extensive gelation during the polymer growth and a high molecular weight polymer [36]. A further limitation of the Gilch pathway, that a number of head–head and tail–tail defects will be built in the structure during the propagation reaction, besides these reasons, they are known to have a detrimental effect on the polymer's opto-electric characteristics.

Olefin metathesis has been employed in the creation of macromolecular materials since the mid-1950s [17,37]. A variant of olefin metathesis known as living ring-opening metathesis polymerization (ROMP) is a powerful method for producing polymers with customizable sizes, shapes, and functionalities. In this approach, Grubbs catalysts—ruthenium complexes—are widely used in the synthesis of block copolymers and in the end functionalization of poly(*p*-phenylene

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Scheme 1. Gilch route to PPV.

vinylene) (PPV) derivatives. This results in polymers with unique topologies, low dispersity, defined regioregularity, and controlled molecular weight.

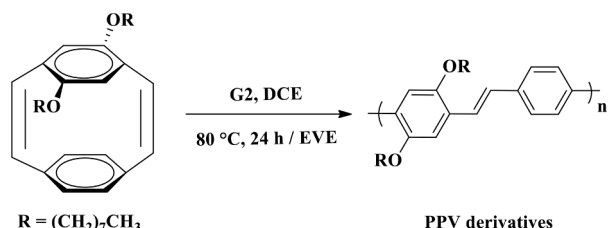
Herein, we report the preparation of the paracyclophanediene (PCPDE) monomer derived from dithia [3.3]paracyclophane through a multi-step reaction that integrates long-chain octyloxy substituents serving as electron-donating and solubilizing groups. Two different methods were employed, with one involving benzyne-induced Stevens rearrangement as a more economical option compared to the Pummerer rearrangement which utilizes the costly 2-(trimethylsilyl)phenyl trifluoromethanesulfonate. The resulting monomer underwent ring-opening metathesis polymerization (ROMP) and was successfully polymerized using the 2nd generation Grubbs catalyst, yielding a well-defined poly(p-phenylene vinylene) (PPV) homopolymer. Subsequently, we present the optical characteristics of this PPV derivative (Scheme 2).

2. Experimental

2.1. Materials, instrumentation and characterization

Unless explicitly stated, all chemicals were utilized in their as-received state from Sigma-Aldrich, Tokyo Chemical Industry, Fujifilm Wako, and Kanto Chemical, without additional purification. Thin-layer chromatography on LC Silica gel 60 F₂₅₄ 25 Aluminium sheets 20 x 20 was employed to monitor the progress of most reactions. Preparative separations were conducted through column chromatography using silica gel Wakosil(R) with a particle size range of 60 to 210 μm . Polymerizations were executed using a Radleys Carousell 12 under a nitrogen atmosphere.

The ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were acquired in deuterated chloroform, and chemical shifts were referenced to tetramethylsilane (TMS) as an internal standard, using a Nihon Denshi JEOL JNM-LA400 spectrometer operating at 400 MHz. Chemical shifts are expressed in parts per million (ppm) relative to the residual solvent peak. All coupling constants (J values) are presented in hertz (Hz), and multiplicity abbreviations such as s (singlet), d (doublet), dt (doublet of triplets), t (triplet), and m (multiplet) are utilized. High-resolution mass spectrometry (HRMS) was conducted on a Nihon Denshi JEOL MStation JMS700. The molecular weights and polydispersity of polymers were determined using Gel Permeation Chromatography (GPC) with a Shodax GPC K-804 L column on a JASCO LC2000 liquid chromatography system, with tetrahydrofuran (THF) serving as the eluent. UV absorption spectra were recorded on a Shimadzu UV-Vis spectrometer 1240, with a standard concentration of 5 mg/100 ml THF. Fluorescence spectra were measured using JASCO FP-8600 fluorometer.



Scheme 2. DO-PPV derivatives Using the Grubbs 2nd Generation Catalyst.

Phosphorescence spectra were recorded on a Hamamatsu Photonics PMA12 C10027-01 with a 340 nm LED (Thorlabs M340L5) as the excitation source. Cyclic voltammogram traces were recorded using a conventional three-electrode configuration with an electrochemical analyzer (ECstat-302, EC frontier, JPN) with a glassy carbon (7.07 mm²) working electrode, a Pt wire counter electrode, and Ag/Ag⁺ reference electrode, and the ferrocene/ferrocenium (Fc/Fc⁺) external reference. Acetonitrile was used as solvent and 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) was used as the supporting electrolyte. The detailed experimental procedure, along with spectral data, for the synthesis of the paracyclophanediene monomer is outlined in the Supporting Information.

2.2. Synthesis of 1,4-bis(dioctyloxy)benzene compound 1

A mixture of 1,4-hydroquinone (20.00 g, 0.1816 mol), 1-bromooctane (87.69 g, 0.4540 mol), and potassium carbonate (62.75 g, 0.4540 mol) was refluxed in acetonitrile (200 ml) for about 48 h. The resultant mixture was cooled followed by stirred in de-ionized water for 30 min at room temperature to afford a dark brown precipitate which collected, washed several times by de-ionized water and dried at 50 °C. Then, the crude material was purified by dissolving in the minimum amount of hot hexane and re-precipitated by using excess of stirred methanolic solution to produce a brown precipitate which filtered, washed with methanol, and dried at 50 °C to give a pale brown solid in (53 g, 80 %) yield. EI-MS calculated for C₂₂H₃₈O₂ m/z : 334.00; Found: m/z 334.00. ^1H NMR (400 MHz, Chloroform-d) δ 6.81 (d, J = 0.4 Hz, 4H), 3.89 (t, J = 6.6 Hz, 4H), 1.75 (dq, J = 8.3, 6.7 Hz, 4H), δ 1.53–1.23 (m, 20H), 0.94–0.84 (m, 6H) ppm. ^{13}C NMR (101 MHz, Chloroform-d) δ 153.30, 115.49, 68.77, 31.90, 29.47, 26.15, 22.74, 14.17 ppm (Figure S1).

2.3. Synthesis of 1,4-bis(bromomethyl)-2,5-bis(octyloxy)benzene compound 2

A mixture of product 1 (21.29 g, 0.1195 mol), paraformaldehyde (7.35 g 0.2451 mol) was dissolved in (300 ml) acetic acid. A solution of hydrobromic acid (42.5 ml) (33 wt.% in acetic acid) was added and the mixture was stirred for 6 h under refluxing system. The reaction mixture was cooled to RT and the suspension was poured onto de-ionized water, the precipitate was isolated by filtration and washed with de-ionized water. The dark brown residue was dissolved in hot chloroform, then poured onto methanol to form a solid white precipitate, which can be repeated for a white loose solid in (28 g, 75.5 %) yield. EI-MS calculated for C₂₄H₄₀Br₂O₂ m/z : 520.00; Found: m/z 520.14. ^1H NMR (400 MHz, Chloroform-d) δ 6.85 (s, 2H), 4.53 (s, 4H), 3.98 (t, J = 6.4 Hz, 4H), 1.81 (dq, J = 8.2, 6.5 Hz, 4H), 1.63–1.21 (m, 20H), 0.98–0.73 (m, 6H) ppm. ^{13}C NMR (101 MHz, Chloroform-d) δ 150.77, 127.62, 114.77, 69.12, 31.90, 29.41, 28.83, 26.16, 22.75, 14.19 ppm (Figure S2).

2.4. Synthesis of 1,4-Benzenedimethanethiol compound 3

A deoxygenated ethanolic solution (200 ml) containing 1,4-Bis(dibromomethyl)benzene (17.8 g, 0.056 mol) and thiourea (9.8 g, 0.13 mol) was refluxed for 5 h to give a suspension which cooled to room temperature and the solvent was removed in vacuo. A solution of deoxygenated water (200 ml) containing Sodium hydroxide (12.6 g, 0.22 mol) was added to the residue followed by refluxing for 2 h. The reaction mixture was cooled to room temperature, neutralized with 50 % aqueous H₂SO₄, and extracted with chloroform (3 \times 100 ml). The organic layer was dried over MgSO₄, filtered, and the solvent removed in vacuo. The resulting solid was crystallized form mixed solution of (chloroform / methanol) to afford a white powder in (9 g, 94 %) yield. EI-MS calculated for C₈H₆S₂ m/z : 170.00; Found: m/z 170.00. ^1H NMR (400 MHz, Chloroform-d) δ 7.3 (d, 4H), 3.69 (d, J = 7.9 Hz, 4H) ppm. ^{13}C NMR (101 MHz, Chloroform-d) δ 140, 128, 22.75 ppm (Figure S3).

2.5. Synthesis of thiacyclophane compound 4

Compound 2 (10 g, 0.019 mol) and Compound 3 (3.27 g, 0.019 mol) were dissolved in deoxygenated benzene (500 ml). This solution was

added extremely slowly dropwise using a pressure-equalizing dropping funnel to a stirred solution of Potassium Hydroxide (4.31 g, 0.077 mol) in deoxygenated ethanol (1000 ml), over 72 h at RT. After a further 3 h, the solvent was evaporated, the residue dissolved in chloroform and

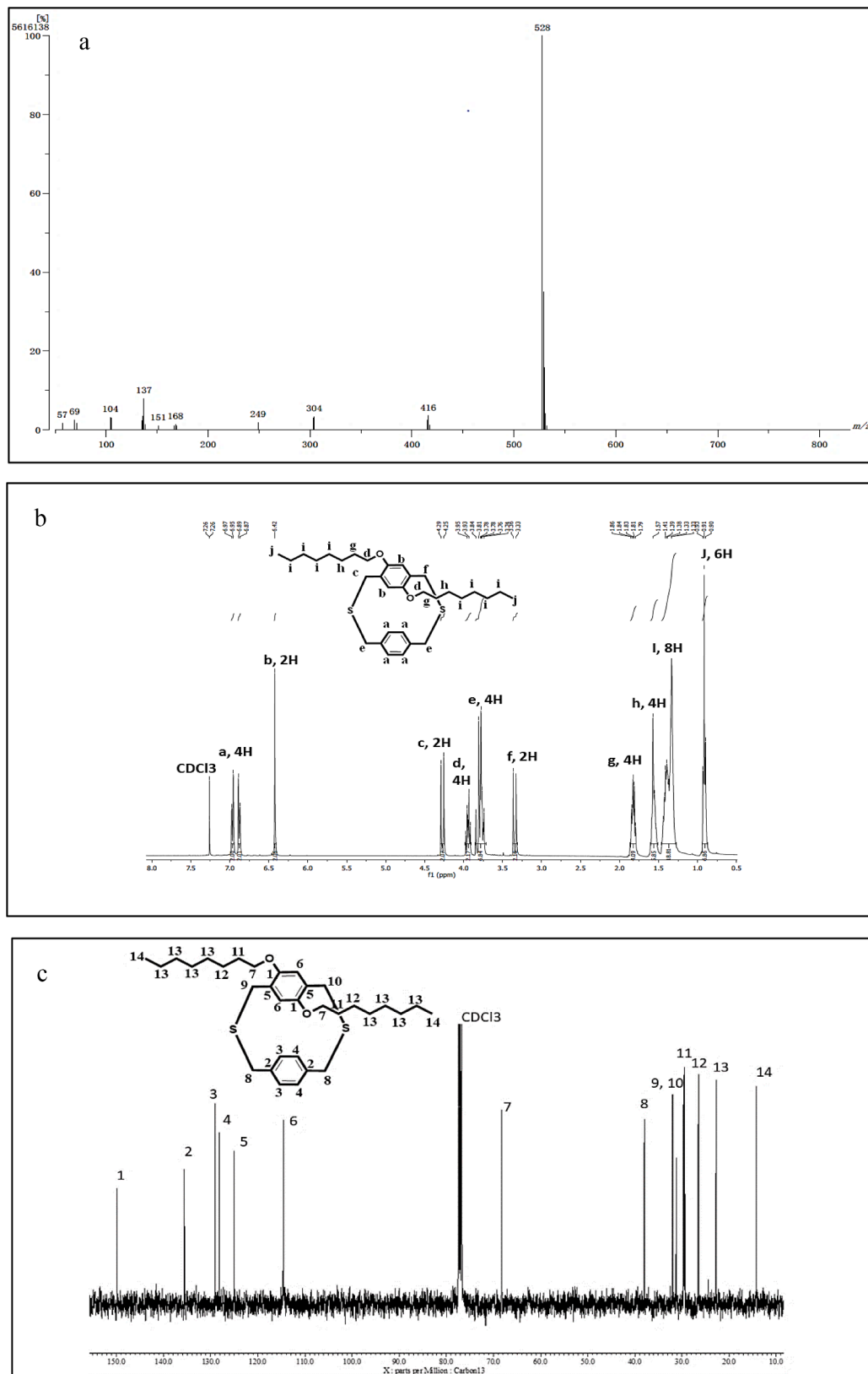


Fig. 1. a) EI-MS spectrum; b) ^1H NMR spectrum; c) ^{13}C NMR spectrum.

water, washed with water and brine in an organic layer which dried by using anhydrous Na_2SO_4 , and the solvent evaporated to give a yellow oil which purified using column chromatography (CHCl_3 : Hexane, 20:80) yielding a colorless oil (6.31 g, 62 %). EI-MS calculated for $\text{C}_{32}\text{H}_{48}\text{O}_2\text{S}_2$ m/z : 528.00; Found: m/z 528.8. ^1H NMR (400 MHz, Chloroform- d) δ 6.92 (dd, $J = 36.7, 7.8, 2.0$ Hz, 4H), 6.42 (s, 2H), 4.28 (d, $J = 14.8$ Hz, 2H), 3.94 (t, $J = 9.2, 6.5$ Hz, 4H), 3.87–3.72 (m, 4H), 3.35 (d, $J = 14.8$ Hz, 2H), 1.82 (dd, $J = 13.2, 7.1, 4.3$ Hz, 4H), 1.57 (dp, $J = 12.8, 4.0$ Hz, 4H), 1.48–1.29 (m, 8H), 0.97–0.87 (m, 6H) ppm. ^{13}C NMR (101 MHz, Chloroform- d) δ 149.82, 135.62, 129.08, 128.23, 124.93, 114.46, 68.20, 38.02, 32.03, 31.22, 29.61, 26.55, 22.83, 14.29 ppm (Fig. 1).

2.6. a. Benzyne-induced Pummerer rearrangement of compound 5

A mixture of the DO-Thiacyclophane 4 (1 g, 0.0037 mol) and 2-(trimethylsilyl) phenyltrifluoromethanesulfonate (1.4 g, 0.0094 mol) in dry THF (100 ml) was stirred at room temperature for few minutes. Then, a solution of Tetrabutylammonium fluoride trihydrate ($\text{TBAF}\cdot 3\text{H}_2\text{O}$) (1.78 g, 0.009189 mol) in dry THF (10 ml) added dropwise using over a period of 5 h. The resulting solution stirred for 1 additional hour then evaporated to produce brown oil. The crude material was purified by column chromatography (CHCl_3 : Hexane, 30:70) yielding a pale yellow oil (1.2 g, 94 %). EI-MS calculated for $\text{C}_{44}\text{H}_{56}\text{O}_2\text{S}_2$ m/z : 680.00; Found: m/z 680.01 (Figure S5).

2.6. b. Benzyne induced Stevens rearrangement compound 6

The DO-Thiacyclophane 4 (3.57 g, 0.00675 mol) and Anthranilic acid (2.77 g, 0.02 mol) were dissolved in anhydrous 1,2-Dichloroethane (100 mL) and heated to 90 °C under nitrogen with a condenser. At the reflux point, Isoamyl nitrite (3.16 g, 0.027 mol) was added by syringe very slowly over a period of at least 60 min. The resulting solution was heated at 90 °C for 1 additional hour and then evaporated to produce brown oil. The crude material was purified by column chromatography (DCM: Hexane, 30:70) yielding a pale yellow oil (1.5 g, 42 %). EI-MS calculated for $\text{C}_{44}\text{H}_{56}\text{O}_2\text{S}_2$ m/z : 680.37; Found: m/z 680 (Figure S6).

2.7. a. Oxidation of phenyl sulfides of compound 7

Stirring the rearrangement product 5 (1.2 g, 0.0018 mol) in chloroform (15 ml) and the solution maintained at 0 °C. After that, a solution of 3-Chloroperoxybenzoic Acid (*m*-CPBA) (0.6 g, 0.0035 mol) was slowly added over approximately 10 min and the reaction mixture stirred for an additional 30 min at 0 °C. Then, quenched by a saturated sodium bicarbonate solution followed by extracted via chloroform, collected the organic phase and washed with de-ionized water (3×100) and dried by anhydrous MgSO_4 , and evaporated to give a (1.25 g, 96 %) yield of the desired product as a clear yellow oil. EI-MS calculated for $\text{C}_{44}\text{H}_{56}\text{O}_4\text{S}_2$ m/z : 712.00; Found: m/z 712.05 (Figure S7).

2.7. b. Oxidation of phenyl sulfides of compound 8

The Stevens rearrangement product 6 (0.75 g, 0.0011 mol) was dissolved in a mixture of benzene (30 ml) and acetic acid (5 ml). The mixture was stirred for 10 min and then cooled to approximately 0 °C using an ice bath. Hydrogen peroxide (0.112 g, 0.0033 mol) was dissolved in acetic acid (5 ml) and added dropwise by syringe over a period of 30 min in air. The vessel was allowed to warm to room temperature and stirred for 12 h in air. Then, quenched by a saturated sodium bicarbonate solution followed by extracted via chloroform, collected the organic phase and washed with de-ionized water (3×100) and dried by anhydrous MgSO_4 , and evaporated to give a (0.355 g, 46.6%) yield of the desired product as a clear yellow oil. EI-MS calculated for $\text{C}_{44}\text{H}_{56}\text{O}_4\text{S}_2$ m/z : 712.05; Found: m/z 712.00 (Figure S8).

2.8. a. Synthesis of substituted [2.2]paracyclophane-1,9-diene (PCPDE) compound 9

Heating under reflux a mixture of compound 7 (0.7 g, 0.00098 mol) and Cs_2CO_3 (1.3 g, 0.0039 mol) was dissolved in *o*-xylene for 4 h. The reaction was cooled, filtered, and solvent removed to form a dark brown oil, which was then purified using column chromatography (CHCl_3 : Hexane, 10:90) to afford a colorless viscous oil in (0.3 g, 75 %) yield, EI-MS calculated for $\text{C}_{32}\text{H}_{44}\text{O}_2$ m/z : 460.00; Found: m/z 460.70. ^1H NMR (400 MHz, Chloroform- d) δ 7.06–6.95 (m, 2H), 6.85 (d, $J = 10.0$ Hz, 2H), 6.67–6.60 (m, 2H), 6.58–6.51 (m, 2H), 5.52 (s, 2H), 3.58–3.43 (m, 4H), 1.54–1.39 (m, 4H), 1.32–1.00 (m, 20H), 0.68–0.60 (m, 6H) ppm. ^{13}C NMR (101 MHz, Chloroform- d) δ 152.46, 138.34, 135.62, 134.54, 131.43, 129.18, 127.61, 120.40, 69.21, 31.96, 29.71, 26.31, 22.78, 14.23 ppm (Fig. 2).

2.8. b. Synthesis of substituted [2.2]paracyclophane-1,9-diene (PCPDE) compound 10

The oxidation product 8 (0.36 g, 0.000505 mol) was dissolved in DMF (40 ml) the mixture was stirred at room temperature for 5 min. The solution was then heated to 155 °C with a nitrogen stream for a period of 20 h. The solution was allowed to cool and washed with dilute aqueous HCl and extracted into chloroform, dried with sodium sulfate to give a yellow oil. The crude material was purified using column chromatography (DCM: Hexane, 10:90) to afford a colorless viscous oil in (0.22 g, 61%) yield, EI-MS calculated for $\text{C}_{32}\text{H}_{44}\text{O}_2$ m/z : 460.00; Found: m/z 460.70. ^1H NMR (400 MHz, Chloroform- d) δ 7.10 (d, $J = 10.1$ Hz, 2H), 6.89 (d, $J = 10.1$ Hz, 2H), 6.79 (d, $J = 8.2$ Hz, 2H), 6.47 (d, $J = 8.2$ Hz, 2H), 5.76 (s, 2H), 3.70–3.82 (m, 4H), 1.67–1.74 (m, 4H), 1.24–1.56 (m, 20H), 0.86–0.92 (m, 6H), 0.20–0.23 (m, 3H) ppm. ^{13}C NMR (101 MHz, CHLOROFORM- D) δ 152.39, 138.31, 135.60, 134.51, 131.39, 127.58, 127.30, 120.29, 77.43, 77.12, 76.79, 69.15, 31.95, 29.69, 29.52, 29.38, 26.29, 22.78, 14.24 (Fig. 3).

2.9. Synthesis of poly(2,5-dioctyloxy-*p*-phenylenevinylene) 11

In a dry Radley Carousell tube under a nitrogen atmosphere, tetrahydrofuran (10 ml) solution containing DO-PCPDE monomer (0.30 g, 6.5118×10^{-4} mol) was stirred for 10 min at 60 °C to fully dissolve. Then, Grubbs 2nd generation catalyst (18.42 mg, 2.1706×10^{-5} mol) was dissolved in dry Tetrahydrofuran (2 ml) under nitrogen and was quickly transferred by syringe to the polymerization vessel, then, the mixture was stirred at 60 °C for 24 h. The mixture was then allowed to cool to RT, and the polymerization was quenched by adding excess ethyl vinyl ether (2 ml). The reaction mixture was allowed to proceed for additional 1 hour. In order to remove the deactivated catalyst the polymerization mixture was passed through silica, the solvent was removed, and the pure polymer was dried in a vacuum oven at 40 °C for 12 h. The pure product will be exposed to 365 nm light to convert the *cis-trans* structure in the polymer to the all-trans structure (Fig. 4b).

^1H NMR (400 MHz, Chloroform- d) δ 7.53–7.49 (m, 2H), 7.33 (d, 3H), 7.25 (s, 3H), 7.21 (d, $J = 4.4$ Hz, 2H), 7.09 (d, $J = 16.7$ Hz, 2H), 6.98 (s, 2H), 6.86–6.44 (m, 6H), 3.97 (t, $J = 6.9$ Hz, 4H), 3.71 (t, $J = 7.3$ Hz, 4H), 1.47–1.38 (m, 24H), 0.83 (t, $J = 26.3$ Hz, 6H) (Fig. 4a).

3. Results and discussion

Scheme 3 illustrates the steps involved in producing the [2.2] paracyclophane-1,9-diene (PCPDE) monomer. In order to prevent the formation of oligomers and polymers, an equimolar amount of 1,4-bis(bromomethyl)–2,5-bis(octyloxy)benzene 2 and 1,4-Benzenedimethanethiol 3 were cyclized at a high dilution in the presence of aqueous potassium hydroxide for at least three days. This process produced the intermediate material, dithiaparacyclophane 4. The benzyne rearrangement of compound 4 using benzyne-induced rearrangement

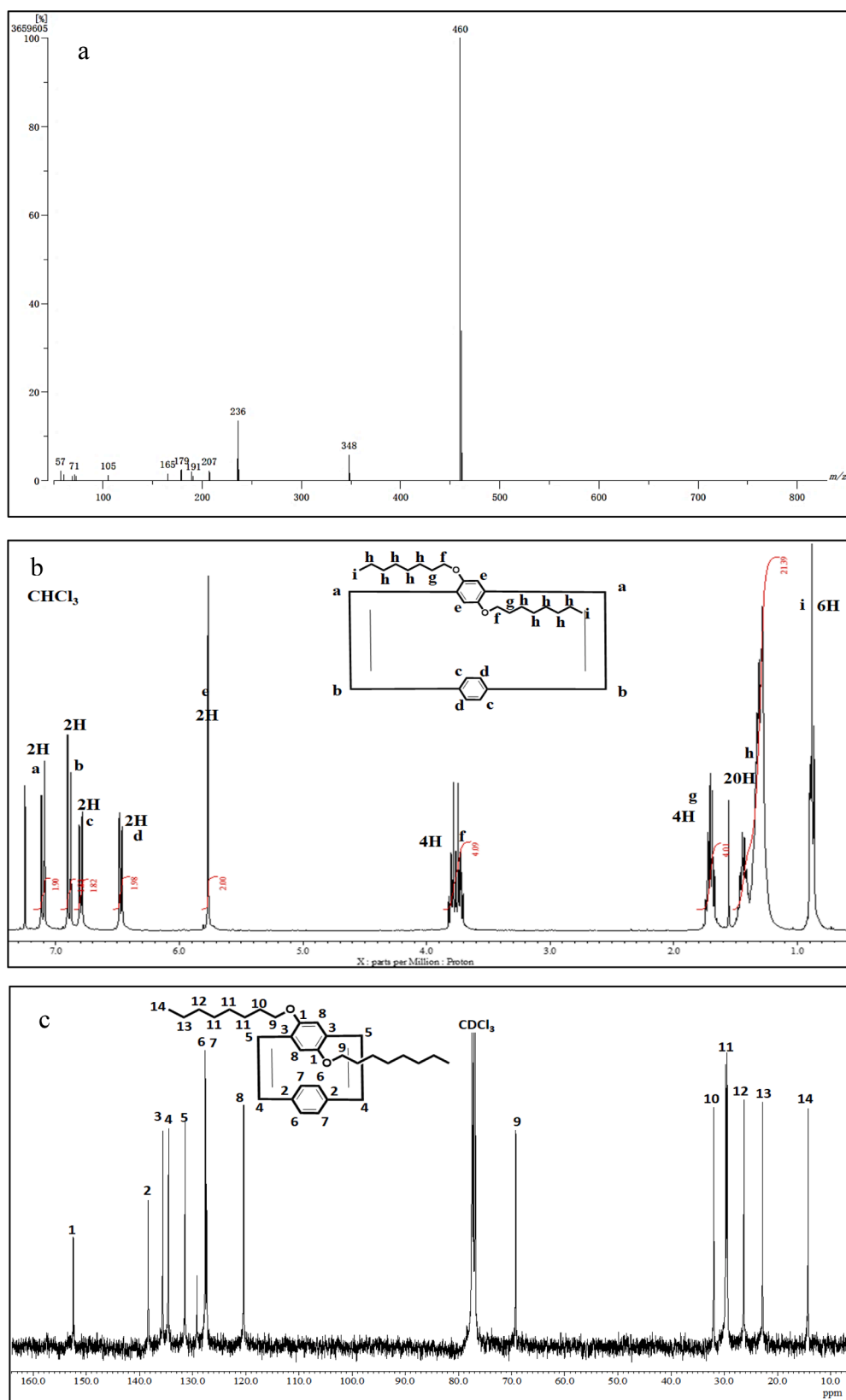


Fig. 2. a) EI-MS spectrum; b) ^1H NMR spectrum; c) ^{13}C NMR spectrum.

Pummerer and Stevens methods also yielded bisphenylsulfides. Compound 5 and 6 were obtained with a yield of 94 % and 42 % respectively after purification via flash column chromatography. Characterizing the mixture of isomers by NMR spectroscopy was challenging due to a large

number of overlapping signals. The ESI mass spectrum of the benzyne rearrangement products exhibited a molecular ion at m/z 680 for both methods.

Compound 7 was synthesized by treatment with *m*-CPBA to give

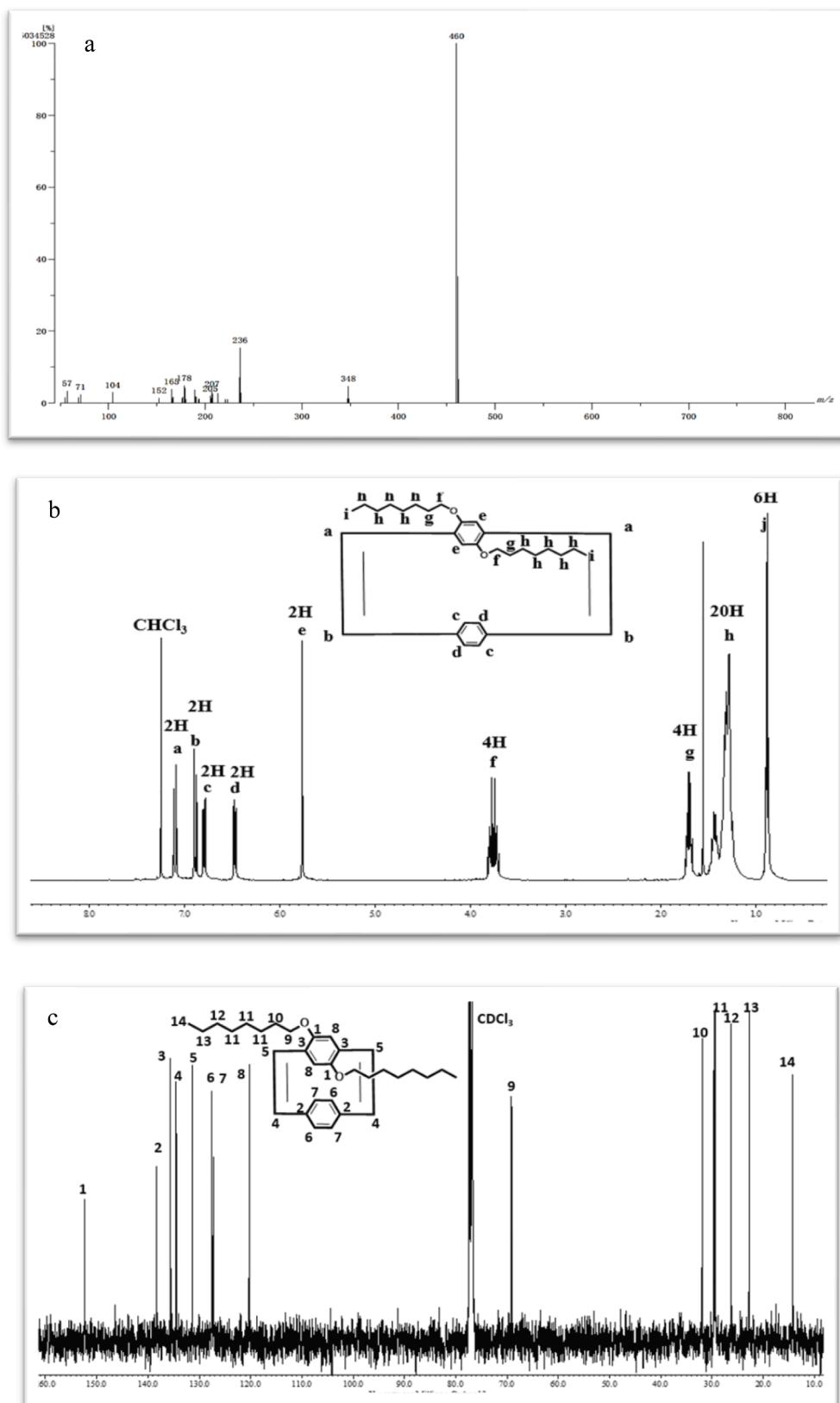


Fig. 3. a) EI-MS spectrum; b) ^1H NMR spectrum; c) ^{13}C NMR spectrum.

corresponding disulfoxides. Then, Compound 7 was heated at reflux in *o*-xylene with Cesium Carbonate. Following purification by column chromatography and recrystallization, a 75 % yield of the (PCPDE) monomer 9 was obtained. Oxidation of the phenyl sulfides by treatment

with 35% w/w hydrogen peroxide in a 1:6 ratio of acetic acid/benzene solution gave the desired bis(sulfoxide) compound 8. Pyrolysis of the bis(sulfoxide) mixture was carried out in DMF solution under reflux with a nitrogen purge for 20 h, and the crude compound was then

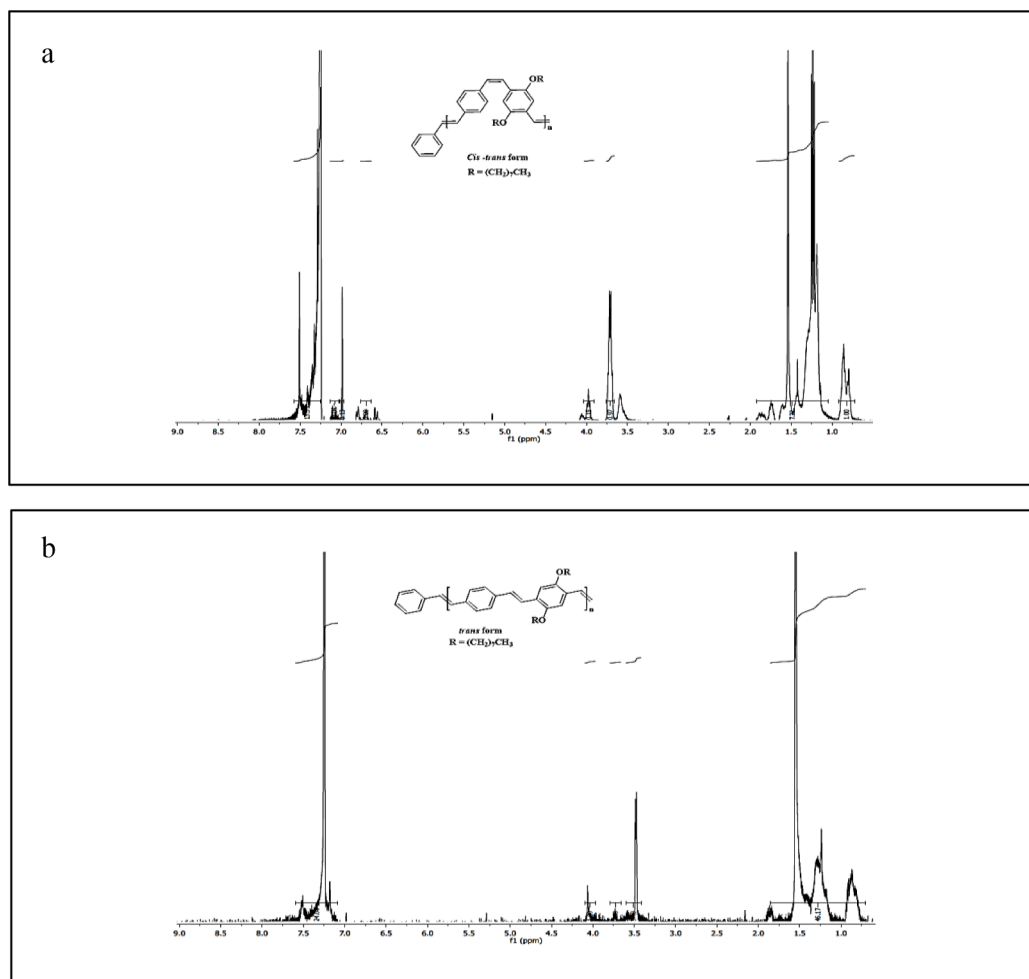


Fig. 4. a) ^1H NMR spectrum of *cis* and *trans* structure. b) ^1H NMR spectrum of *trans* structure.

chromatographed in hexane to give the (PCPDE) monomer **10** in an overall yield of 46.6 %. Then the monomer followed by the polymerization process utilizing Grubb's 2nd generation catalyst, and it was ultimately quenched by adding excess ethyl vinyl ether (Scheme 2)

Fig. 2b illustrates the ^1H NMR spectrum of the DO-PCPDE monomer **9** in chloroform- d . Four doublets corresponding to the *cis*-vinyl hydrogens were observed at chemical shifts of 7.06, 6.95, 6.85, and 6.67 ppm. Two additional doublets were attributed to the hydrogens of the substituted phenyl ring at 6.95 and 6.41 ppm. Additionally, the hydrogens in the non-substituted phenyl ring manifested as a doublet at 6.47 ppm, integrating two hydrogens. One of the two aromatic hydrogens of the substituted phenyl ring appeared as a singlet at 5.52 ppm. Signals below 2 ppm in all three spectra corresponded to hydrogens of the long alkyl chain, except for methylene hydrogens linked to oxygen atoms. Furthermore, Fig. 2a exhibited a peak with a molecular weight of 460 (M^+) visible in the EI-MS analysis, indicative of the full formation of the desired monomer **9**. Similarly, monomer **10** exhibited nearly identical data in Fig. 3. Fig. 4 (a and b) display the polymer's ^1H NMR spectra. The peaks at 3.97 and 3.71 ppm, respectively, are the methylene hydrogens bound to the oxygen adjacent to the *trans*- and *cis*-vinylenes. At 6.86 and 6.44 ppm, the signals of hydrogens for *cis*-vinylene and *o*-phenyl to the *cis*-vinylene were detected. Furthermore, peaks corresponding to the hydrogens for *trans*-vinylene and *o*-phenyl for *trans*-vinylene are seen at 7.53 and 7.49 ppm, respectively.

As shown in Fig. 5, the polymer exhibited a reasonable number-average molecular weight (M_n) value of 181,332 g/mol and a weight-average molecular weight (M_w) value 215,196 g/mol obtained from GPC analysis. So, the polydispersity index (PDI) can be calculated as

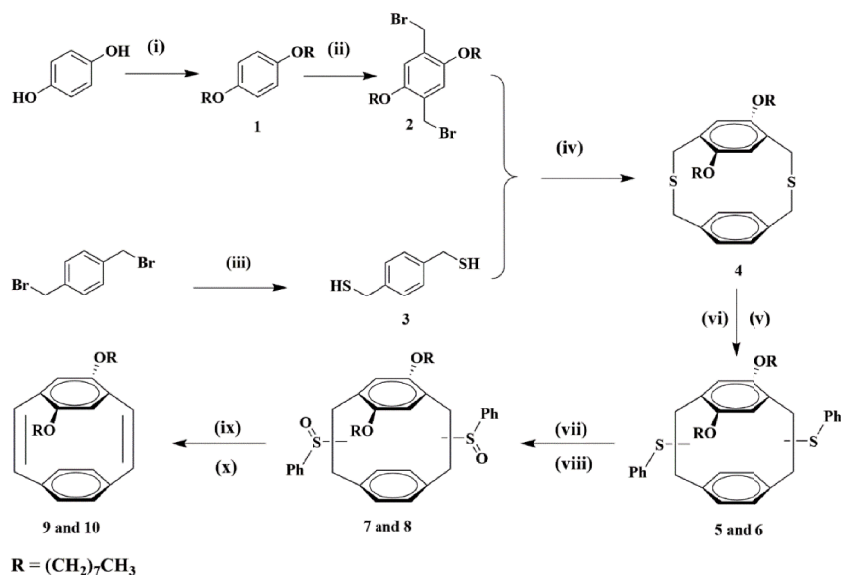
1.22 with yield 91 %. It can be generally considered to be a narrow molecular weight distribution, which is important for use in electronic and optoelectronic applications, such as solar cells, light-emitting diodes, and field-effect transistors, where their good film forming properties are highly dependent on their molecular weight and the uniformity of their structure

In these applications, a low PDI value is desirable, as it can lead to more consistent and stable electronic properties in the final device with minimal quenching. Additionally, a comparison analysis was conducted on the end products of the polymer produced through ROMP and the Gilch method [36,38,39]. The findings indicated that the PPV derivative obtained exhibited superiority in terms of PDI, polymer purity, yield, and applications such as OLEDs.

The PPV derivative absorption spectra were measured in the variable solutions including CHCl_3 , $\text{C}_6\text{H}_5\text{Cl}$, and THF. Furthermore, a detailed illustration of thin film casting on a glass slide was provided Figures (6-8) and Table 1 provides a summary of associated optoelectronic properties. UV-vis absorption maxima (λ_{max}) in the range of 470.90 – 485.70 nm were shown by the PPV in varied solutions. As presented major absorption peaks for CHCl_3 and $\text{C}_6\text{H}_5\text{Cl}$ have been found at 470.90 and 485.70 nm, correspondingly (Fig. 6).

Remarkably, THF had strong band of absorption at 485.00 nm in addition to its tiny shoulder peaks at 515.00 nm. The thin-film UV-vis absorption of PPV derivatives emerged (Fig. 7). In this instance, the PPV homopolymer showed a broader band compared to the solution because of the polymer chains solid-state aggregation [40], and (λ_{max}) values were discovered at 480.16 nm.

The photoluminescence emission spectra of the homo-polymerized



(i) 1-bromooctane, K_2CO_3 , HBr, Acetonitrile, 80 °C, 48 h; (ii) Paraformaldehyde, Acetic acid, 70 °C, 6 h; (iii) a-Thiourea, Ethanol, 90 °C, 5 h; b- KOH (aq.), 110 °C, 2 h; c- H_2SO_4 , RT, 1 h; (iv) KOH (alc.), Benzene, RT, 72 h; (v) TBAF, TMS-PTFMS, Dry THF, RT, 6 h; (vi) anhydrous 1,2-dichloroethane, isoamyl nitrite, anthranilic acid, under N_2 , 90 °C, 2 h; (vii) *m*-CIPBA, Chloroform, 0 °C, 1 h, (viii) Benzene / acetic acid, H_2O_2 , RT, 12 h; (ix) Cs_2CO_3 , *o*-xylene, 150 °C, 20 h; (x) DMF, nitrogen stream, 155 °C, 20 h

Scheme 3. Synthesis of Paracyclophanediene Monomer.

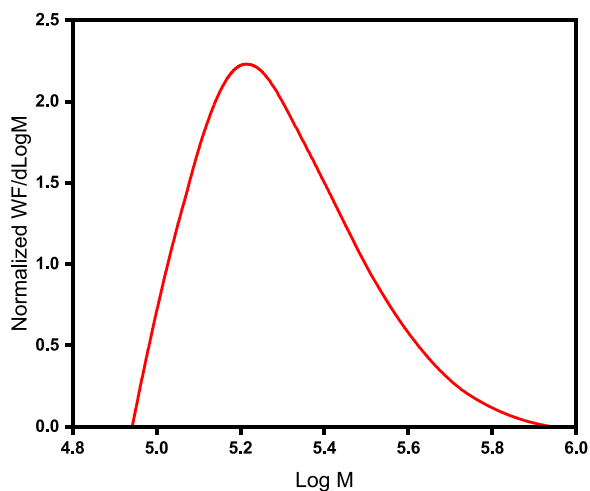


Fig. 5. Molecular weight distribution of polymer.

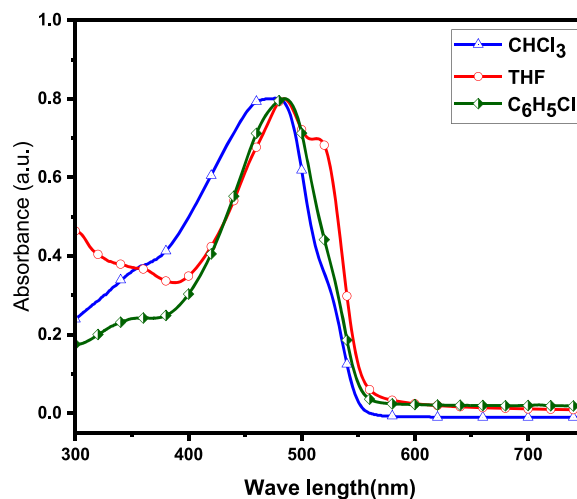


Fig. 6. Absorption profile of the polymer.

synthesized PPV derivative were obtained by irradiative excitation at their respective wavelengths of the absorption maximum in variable solutions at concentrations 10^{-6} M at room temperature. In addition, the casting thin film is provided in Fig. 7, and their data are displayed in Table 1. The highest emission bands in various solutions were observed in the region of approximately 539.0–555.8 nm. When CHCl_3 was stimulated at λ_{max} (470.00 nm), the λ_{em} maximum (558.65 nm) was reached. Hence in this instance, THF and $\text{C}_6\text{H}_5\text{Cl}$ share the identical excited λ_{max} at 480.00 nm in addition to having respective λ_{em} maximum values of 539.07 nm and 545.00 nm (Fig. 8). Furthermore, the emission maximum λ_{em} was noticed at (647.85 nm) when the thin film was included at the excited λ_{max} (480 nm), and noticed that, in comparison to the emission maxima of different solutions, the λ_{em} in the thin film was more-red shifted, so this observation suggests that reduce the energy gap

between the relaxed S^1 and S^0 .

Therefore, the optical band gap (E_g^{op}) of the PPV derivative was determined by two methods one of those using the absorption onsets (λ_{onset}) according to this equation: $(E_g^{\text{op}}) = 1240/\lambda_{\text{onset}}$ in addition to Tauc plot Fig. 9. The onsets thin film in addition to, onsets of CHCl_3 , $\text{C}_6\text{H}_5\text{Cl}$, and THF absorptions (λ_{onset}) of PPV derivative was estimated to be near 561.01, 551.06, 552.80 and 556.70 nm, respectively. Therefore, their E_g^{op} was anticipated to be among 2.21 - 2.25 eV. On the other hand, the Tauc plot E_g^{op} approach estimates a trend by linearly extending to zero of the linear regions of the $(\alpha h\nu)^{1/2} = f(h\nu)$ curves. In which $h\nu$ is the energy of the photon and α is the absorption coefficient. Additionally, the Tauc plot was represented in the range of 2.07 to 2.19 and Table 1 displays the E_g^{op} for both thin-film and variable solutions.

The polymer's electrochemical characteristics were assessed via

Table 1
Optical properties of the polymer.

	Sample	U.V- Vis Absorption		E_g^{op} (eV)		Fluorescence Emission	
		λ_{max} , nm	λ_{onset} , nm	Onset absorption edge	Tauc plot	λ_{ex} , nm	λ_{em} , nm
Solution	CHCl ₃	470.90	551.06	2.25	2.17	530	558.65
	C ₆ H ₅ Cl	485.70	552.80	2.24	2.19	530	539.07
	THF	485.00	556.70	2.23	2.18	530	545.00
Thin film		480.16	561.01	2.21	2.07	600	647.85

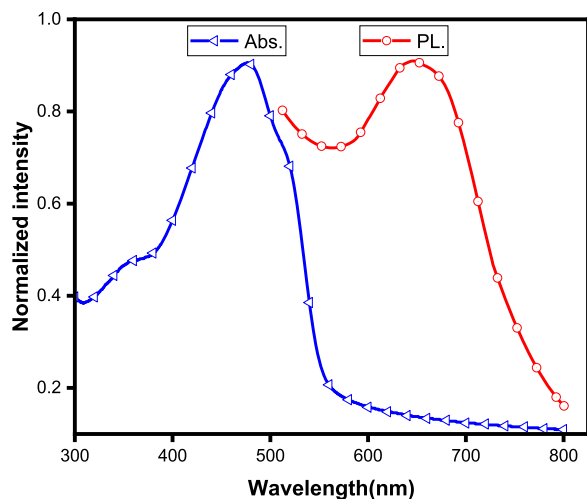


Fig. 7. Thin film Absorption and emission.

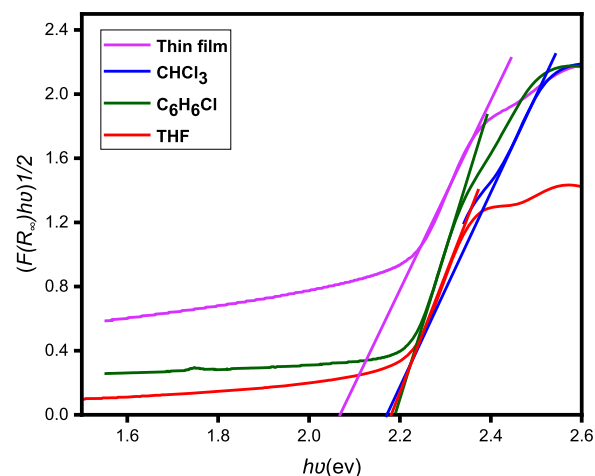


Fig. 9. Tauc plot band gab.

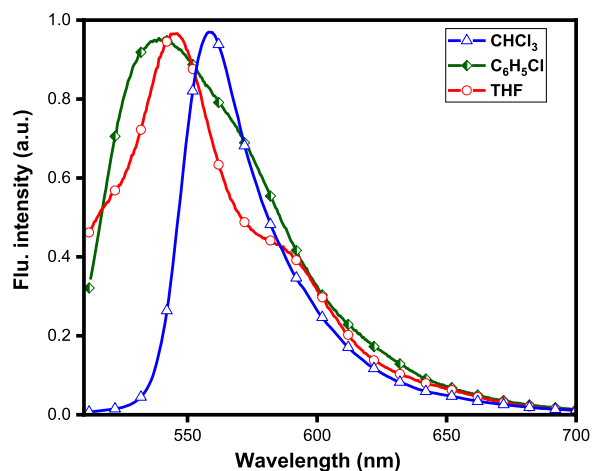


Fig. 8. Emission profile of the polymer.

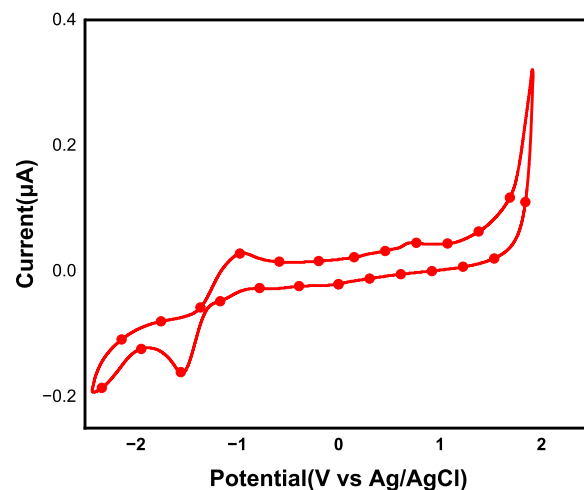


Fig. 10. Cyclic voltammograms for polymer on a Pt electrode in an acetonitrile solution containing 0.1 M NBu₄PF₆.

cyclic voltammetry in solid-state conditions, employing tetrabutylammonium hexafluoride in acetonitrile (0.1 M) as the electrolyte. The polymer films were deposited onto a glassy carbon working electrode. The estimated energy levels for E_{HOMO} and E_{LUMO} are approximately -5.94 and -3.58 eV, respectively (Fig. 10).

By applying the equation for the difference between the HOMO and LUMO energy levels, we determined that the electrochemical band gap is 2.37 eV, which closely aligns with the energy obtained from the optical band gap [34,41].

4. Conclusion

The diocyloxy-substituted [2.2] paracyclophane-1,9-diene was

synthesized efficiently in three steps from the respective dithiacyclophane using induced-benzyne Stevens rearrangement, which proved to be a more cost-effective method compared to induced-benzyne Pummerer rearrangement. This was followed by oxidation and thermal elimination processes. Subsequently, the monomer underwent polymerization by the Grubbs 2nd generation catalyst using ROMP technique, resulting in a soluble DO-PPV polymer with low polydispersity. Characterization of the synthesized components was achieved using high-resolution mass spectrometry and nuclear magnetic resonance spectroscopy.

Moreover, the optical properties of the resulting polymer, including UV and photoluminescence, were explored in both solution and thin-

film states. The photophysical studies revealed that these polymers exhibit effective light absorption between 470.90 – 485.70 nm in solutions and at 480.16 nm in thin film, indicating favorable energy band gaps. Additionally, they displayed intriguing fluorescence emission maximum (λ_{em}) in solution, reaching up to 558.65 nm. In contrast, the thin film exhibited a distinct red shift, extending up to 647.85 nm, making it a promising candidate for organic light-emitting materials.

CRedit authorship contribution statement

Mahmoud Z. Basyouni: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. **Mohamed E. Abdu:** Writing – review & editing, Writing – original draft, Visualization. **Mohammed F. Radwan:** Writing – review & editing, Writing – original draft, Visualization. **Andrew M. Spring:** Writing – original draft, Supervision, Software, Resources, Project administration, Investigation, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

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

Data availability

No data was used for the research described in the article.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.molstruc.2024.138001](https://doi.org/10.1016/j.molstruc.2024.138001).

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