Phenoxazine and diketopyrrolopyrrole based donor-acceptor conjugated polymers: synthesis and optical properties

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Abstract

While numerous phenoxazine-based small molecules developed for organic electronic devices, very limited attention has been received on synthesized conjugated polymers containing this phenoxazine. Herein, we designed and synthesized two new low-bandgap donor−acceptor conjugated copolymers based on phenoxazine with different side chains and diketopyrrolopyrrole by Pd-catalyzed direct (hetero)arylation polycondensation using a $Pd(OAc)_2$ catalyst and PCy_3. HBF_4 ligand. The effects of side chain branched alkyl and benzoyl of phenoxazine on the thermal, and optical properties of the polymers have been investigated. Both the polymers have a good yield 85%, high molecular weight up to 41500 g/mol, low dispersity index 1.91, excellent solubility in common organic solvents, and a broad absorption spectrum in the range of 500-900 nm with optical bandgaps as low as 1.40 eV. All these polymers possess good thermal stability with decomposition temperatures over 350 °C and no obvious thermal transitions.

Keywords: *conjugated polymer, donor−acceptor polymer, phenoxazine, diketopyrrolopyrrole, direct arylation polycondensation*

1. Introduction

Over the past 20 years, conjugated polymers have received the most attention as novel organic semiconducting materials to alternative silicon-based devices for organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), and polymer solar cells (PSCs) due to their flexibility, low cost, lightweight, and solution processability[1,2]. Therefore, the discovery of innovative semiconducting polymers is an essential task to develop next-generation electronic devices. Among them, phenoxazine(POZ)-based semiconductors, which include electron-rich nitrogen and oxygen heteroatoms in a heterocyclic structure that results from nonplanar butterfly conformation, have greatly enhanced the device performance. Thus, several small molecules containing POZ are widely used in organic electronic devices[3,4], including OLEDs[5,6], fluorescent probes[7], OSCs and perovskite solar cells[8-10], as well as photoredox catalysts in atom transfer radical polymerization[11]. In contrast to POZ-based small molecules, POZ-based polymers are far less common, hence more research is necessary.

In organic optoelectronic devices, conjugated polymers have clear advantages over small-molecule materials such as flexibility and stretchability[12-14]. Therefore, it is important to develop conjugated polymers with high molecular weights. Since 2005, POZ-based conjugated polymer was first reported by the Jenekhe group[15], several p-type conjugated polymers-based POZ have been synthesized and used in p-channel OFETs and PSCs[16,17]. There have also been some reports on POZ-based ladder polymers that serve as innovative supercapacitor electrode materials[18]. Moreover, most of the reports discussed properties of POZ-based polymers as p-type materials, while a few pieces of literature referred to that in n-type polymer, bearing high coplanarity that leads to a low optical band gap. POZ-based polymers have been synthesized primarily by cross-coupling reactions such as the Suzuki−Miyaura coupling and the Migita−Kosugi−Stille coupling reactions. However, the resulting polymers had low molecular weights with the number-average molecular weight (M_n) lower than 10 000 g/mol due to the instability of the boronated POZ monomer[15,19]. Alternatively, transition metal-catalyzed direct (hetero)arylation polymerization (DArP or DHAP) via C–H bond activation has been developed recently as a new synthetic method for conjugated polymers[20,21]. Because this polycondensation method does

not require an organometallic monomer, the preparation step for a boronated monomer and concern about its instability can be avoided. The absence of organometallic monomers also results in the high purity of the polymers because organometallic monomers do not contaminate waste with metals. The main issue still lies in selecting the appropriate processes to produce high-molecular-weight polymers with high selectivity and broad monomer scope.

In this regard, our group reported highly efficient Pd-catalyzed direct arylation polycondensation of a novel low bandgap POZ-based polymer as a potential photoactive donor material in bulk heterojunction (BHJ) OSCs[17]. Herein, we report further investigation of direct arylation polycondensation of the POZ with different side chains and diketopyrrolopyrrole (DPP) to design and synthesized novel low-bandgap donor-acceptor conjugated copolymers. We also investigated the effect of the side chain on the electronic, optical, and nanostructures properties of the new POZ-based polymers, including poly(10-ethylhexyl phenoxazine-3,7-diyl-alt-3,6-dithien-2-yl-2,5-diethylhexylpyrrolo[3,4-c]pyrrole-1,4-dione-5′,5″-diyl) (**P1**) and poly(10-hexylbenzoyl-phenoxazine-3,7-diyl-alt-3,6-dithien-2-yl-2,5-diethylhexylpyrrolo[3,4-c]pyrrole-1,4-dione-5′,5″-diyl) (**P2**).

2. Materials and Methods

2.1 Materials

All chemical reagents were used without further purification as purchased from Aldrich, Acros, and TCI chemical unless otherwise specified. Phenoxazine (98%), and 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione were purchased from TCI (Tokyo, Japan). Triethylamine (98%), 4-dimethylaminopyridine (98%), 2-ethylhexyl bromide (98%), 4-hexylbenzoyl chloride (98%), and tetrahydrofuran (99.9%) were purchased from Acros Organics. Palladium(II) acetate (Pd(OAc)$_2$, 98%), tricyclohexylphosphine tetrafuoroborate (97%, PCy$_3$·HBF$_4$), and pivalic acid (PivOH, 97%) were purchased from Sigma-Aldrich. Sodium tert-butoxide (NaO-tBu, 97%), sodium carbonate (99%), and magnesium sulfate (98%) were purchased from Acros and used as received. Chloroform (CHCl$_3$, 99.5%), and dimethylacetamide (DMAc, 99%) were purchased from Fisher/Acros and dried using molecular sieves under N$_2$. Dichloromethane (99.8%), hexane (99%), methanol (99.8%), and ethyl acetate (99%) were purchased from Fisher/Acros and used as received.

2.2 Instrumentation

FT-IR spectra collected as the average of 256 scans with a resolution of 4 cm^{-1}, were recorded from KBr disk on the FT-IR Bruker Tensor 27. ^{1}H NMR spectra was carried out on a 500 MHz spectrometer – Bruker AMX500 apparatus in CDCl$_3$. ^{1}H NMR chemical shifts are referenced to TMS (δ 0.00 ppm). The following abbreviations are used to describe the NMR signals: s (singlet), d (doublet), t (triplet), q (quartet), and br (broad). Size exclusion chromatography (SEC) measurements were performed on a Polymer PL-GPC 50 gel permeation chromatograph system equipped with an RI detector, with chloroform as the eluent at a flow rate of 1.0 mL/min, 35 ^{0}C. Molecular weights and molecular

weight distributions were calculated with reference to polystyrene standards. UV–vis absorption spectra of polymers in solution and polymer thin films were recorded on a Shimadzu UV-2450 spectrometer over a wavelength range of 300–900 nm. Fluorescence spectra were measured on a HORIBA IHR 325 spectrometer. Differential scanning calorimetry (DSC) measurements were carried out with DSC 204 F1-NETZSCH instruments under nitrogen flow (heating rate 10 °C min^{-1}). Thermogravimetric analysis (TGA) measurements were performed under nitrogen flow using STA 409 PC Instruments with a heating rate of 10 °C min^{-1} from ambient temperature to 800 °C.

2.3 Synthesis of the monomers and polymers

2.3.1 Synthesis of monomer 10-(2-ethylhexyl)-10H-phenoxazine (M1)

Monomer 10-(2-ethylhexyl)-10H-phenoxazine (M1) was synthesized according modified earlier procedures[8]. A schlenk tube was charged with phenoxazine (400 mg, 2.18 mmol), and sodium tert-butoxide (252 mg, 2.62 mmol) in 10 mL of THF under nitrogen. After the mixture refluxed for 1 h, 2-ethylhexyl bromide (506 mg, 2.62 mmol) was added, then the mixture refluxed for 23 h. After the reaction, the solvent was removed by rotary evaporation, then 30 mL of water are added and the solution is extracted with dichloromethane. Collect the organic layer and the solvent was removed by rotary evaporation. The residue was purified by chromatography (silica gel, hexane) to provide product M1 as a colorless oil (550 mg, 86%). ^{1}H NMR (500 MHz, CDCl$_3$, ppm): δ 6.86 – 6.79 (d, 2H), 6.70 – 6.60 (m, 4H), 6.56-6.50 (d, 2H), 3.41 (d, J = 7.3 Hz, 2H), 1.88 (dd, J = 12.7, 6.4 Hz, 1H), 1.46 – 1.26 (m, 8H), 0.94-0.86 (m, 6H).

2.3.2 Synthesis of monomer 10-(4-(hexyl)benzoyl)-10H-phenoxazine (M2)

4-hexylbenzoyl chloride (587. mg, 2.62 mmol) was placed in a nitrogen-filled round bottom flask equipped with a reflux condenser, phenoxazine (400 mg, 2.18 mmol), 10 mL THF, triethylamine (0.3 mL, 2.18 mmol), and 4-dimethylaminopyridine (45 mg, 0.36 mmol) were added. The mixture was heated to reflux for 72 h. After the reaction, the solvent was removed by rotary evaporation, then 30 mL of water are added and the solution is extracted with dichloromethane. Collect the organic layer and the solvent was removed by rotary evaporation. The residue was purified by chromatography (silica gel, hexane/ethyl acetate: 15/1) to provide product M2 as a colorless oil (512 mg, 75%). ^{1}H NMR (500 MHz, CDCl$_3$, ppm): δ 7.38 (d, J = 7.9Hz, 2H), 7.33 (d, J = 7.3 Hz, 2H), 7.12 (m, J = 7.2 Hz, 4H), 7.07 (d, 2H), 6.93 (d, 2H), 2.57 (m, 2H), 1.59 (m, 2H), 1.38 - 1.18 (m, 6H), 0.87 (m, J = 7.2 Hz, 3H).

2.3.3 General synthesis of donor-acceptor conjugated copolymers P1 and P2 via direct arylation polycondensation

A 25 mL Schlenk flask was charged with monomer **M1** (88.63 mg, 0.3 mmol) or **M2** (111.44 mg, 0.3 mmol), 3,6-bis(5bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (DPP) (204.77 mg, 0.3 mmol) and DMAc (6 mL). The reactor was purged with nitrogen for 20 min. The septum was

opened and Pd(OAc)$_2$ (3.36 mg, 0.015 mmol), PCy$_3$.HBF$_4$ (11.05 mg, 0.03 mmol), PivOH (30.64 mg, 0.3 mmol), and K$_2$CO$_3$ (248.767 mg, 1.8 mmol) were added. Oxygen was removed from the reaction solution by three freeze–pump–thaw cycles, and at the end the reactor was then back-filled with argon to preserve an inert atmosphere. The reactor was heated in a 100 °C oil bath for 4h. After being cooled to room temperature, the reaction mixture was diluted with 30 mL of chloroform. The obtained organic layer was passed through Celite to remove the Pd catalyst and the insoluble polymer fraction, concentrated and was precipitated into methanol. The product was purified by sequential Soxhlet extractions using methanol (6h), acetone (6h), and hexane (6h). The resultant polymer was further purified by dissolving in CHCl$_3$ and reprecipitating into methanol. The pure copolymers were obtained after drying under a vacuum at 60 °C overnight.

P1: a deep blue solid in 82% yield, 201 mg. ^{1}H NMR (500 MHz, CDCl$_3$, ppm): δ 9.1-8.66 (d, 2H), 7.71 (m, 3H), 7.52 (m, 3H), 7.37 (d, 2H), 4.22 (td, 4H), 4.05 (td, 2H), 1.90 (m, 2H), 1.88-1.26 (m, 24H), 0.94-0.86 (m, 18H). GPC: M$_n$ = 28 000 gmol^{-1}, M$_w$/M$_n$ = 2.22.

P2: a deep blue solid in 85% yield, 228 mg. ^{1}H NMR (500 MHz, CDCl$_3$, ppm): δ 9.1-8.66 (d, 2H), 8.65 (d, 2H), 8.46 (d, 2H), 8.44-8.20 (m, 3H), 8.19-7.94 (m, 3H), 7.34 (d, 2H), 4.06 (td, 4H), 2.30 (td, 2H), 1.90 (dd, 2H), 1.75-1.16 (m, 24H), 0.94-0.84 (m, 15H). GPC: M$_n$ = 41 500 gmol^{-1}, M$_w$/M$_n$ = 1.91.

3. Results and Discussions

We synthesized two different donor-acceptor conjugated copolymers based on DPP as an acceptor unit and POZ as a donor unit, in which the effect of replacing the branched alkyl substituent at the POZ by a benzoyl moiety on the structural, photophysical, and thermal parameter was investigated. The synthesis of all monomers (**M1** and **M2**) and their copolymers (**P1** and **P2**) is outlined in Scheme 1.

3.1 Monomer synthesis

First, two monomers POZ, **M1** and **M2,** were synthesized in only one step from relatively inexpensive and commercially available H-phenoxazine with high yields of 86% and 75%, respectively. The structure of monomers **M1** and **M2** was determined via ^{1}H NMR. The ^{1}H NMR spectrum of monomer **M1** (Figure 1a) shows a doublet peak at 6.86 ppm (peak d), a triplet peak at 6.70 ppm (peak b, c), and a doublet peak at 6.56 ppm (peak a) corresponding to the protons of the POZ benzene ring. The peaks from 0.86 ppm to 3.41 ppm are attributed to the ethylhexyl protons. Similarly, the ^{1}H NMR spectrum of monomer **M2** (Figure 1b) also showed all characteristic peaks of the hexylbenzoyl-POZ. The presence of these peaks, along with their integral ratios, indicate that the reaction has taken place successfully to give the ethylhexyl-POZ and hexylbenzoyl-POZ monomers.

3.2 Polymer synthesis

As shown in Scheme 1, the alternating POZ-DPP copolymers were synthesized by direct arylation polycondensation between branched alkyl or benzoyl alkyl of POZ and dibromides of DPP to give **P1**, and **P2**, respectively. The polycondensation was carried out in dimethylacetamide (DMAc) at 100 °C for 4h with 5%mol of Pd(OAc)$_2$, 10%mol of PCy$_3$.HBF$_4$, 1.0 equivalent of pivalic acid (PivOH), and 6.0 equivalents of K$_2$CO$_3$. Both polymers were purified by sequential Soxhlet extractions using methanol (6h), acetone (6h), and hexane (6h) to remove catalyst and oligomers, then a chloroform fraction was collected, precipitated from cold methanol and isolated. The yield of both reactions was a high yield ≥ 82%. All the polymers showed excellent solubility in organic solvents such as tetrahydrofuran, chloroform, toluene, and chlorobenzene at room temperature. The number average molecular weights (M$_n$) and dispersity (Đ) of the two polymers **P1** and **P2** were determined by gel permeation chromatography (GPC) against polystyrene standards in CHCl$_3$ and were found to be 28 000 and 41 500 gmol^{-1} and 2.22 and 1.91, respectively (Table 1).
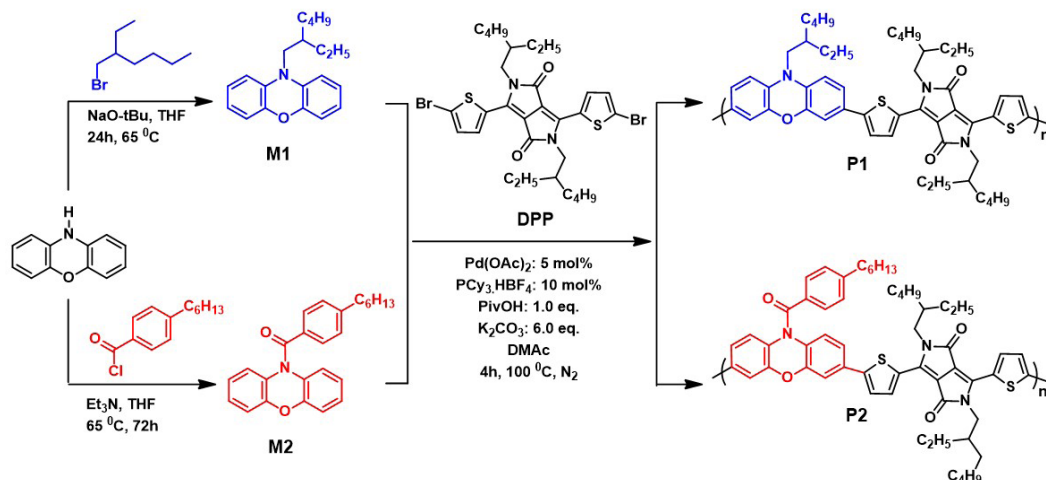

**Scheme 1.** Route of synthesis for the phenoxazine-based monomers and copolymers.

3.3 Polymer structure

The chemical structures of the polymers were verified by FT-IR, and ¹H NMR spectra. Figure 2 shows the FT-IR spectra of the obtained these copolymers. The bands at 2850 and 3060 cm⁻¹ are ascribed to C−H stretching modes of n-alkyl groups and ring C−H stretching vibrations. The vibrational bands between 1550 and 1000 cm⁻¹ in all the polymers are due to stretching vibrations of the C−N

and C−O groups in the phenoxazine ring. Especially, a peak at 1689 cm⁻¹ appears in the spectrum of the **P2** attributed to the stretching vibration of the carbonyl groups (C=O) having higher intensity than of the **P1**. Figure 3 showed the ¹H NMR spectra of the alternating copolymers, **P1** and **P2**, which were in good agreement with the polymers' structures. The spectrum of **P1** showed resonances in the range of 7.5-7.8 ppm that can be attributed to the protons in the
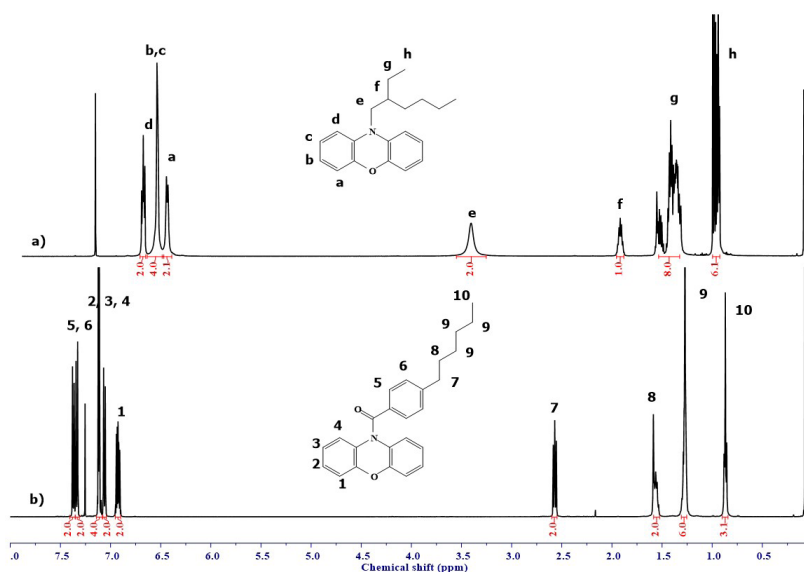
Figure 1. ¹H NMR spectra of monomer **M1** (a) and **M2** (b) in CDCl₃.
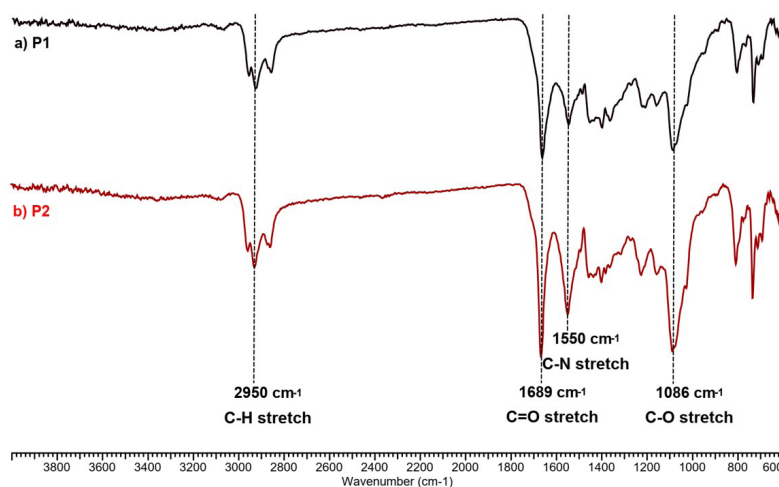
Figure 2. Comparative FT-IR spectra of **P1** (a) and **P2** (b).

Table 1. Polymerization yields, molecular weights and thermal properties of copolymers.

Polymer	Yield (%)	Mn (gmol⁻¹)[a]	Đ[a]	T$_g$ (°C)[b]	T$_d$ (°C)[c]
P1	82	28 000	2.22	-	374
P2	85	41 500	1.91	-	375

[a] Number-average molecular weight and dispersity index (Đ) determined by GPC with CHCl₃ as eluent using polystyrene standards; [b] Glass transition temperature determined by DSC at a heating rate of 10 ⁰C/min under nitrogen; [c] Temperature at 10% weight loss measured by TGA under nitrogen.

phenoxazine ring and peaks at 9.0 ppm and 7.3 ppm which is attributable to the protons in the DPP ring. In contrast, the proton in the phenoxazine ring was represented by the **P2** spectrum peaks at 7.9–8.6 ppm. While the resonance at 4.25 ppm in the spectra of P1 is assigned to the two R-methylene protons in the N-substituted hexyl chain, the peak at 2.26 ppm in the **P2** spectrum corresponds to the two R-methylene protons in the N-benzoyl hexyl chain.

The thermal properties of the polymers were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen and the results are summarized in Table 1 and Figure 4. All the polymers showed good thermal stability with the onset decomposition temperature (T_d) weight loss of 10% occurred above 350 °C and a loss of about 50 wt% at 800 °C (Figure 4a). No obvious thermal transitions were detected in the second heating scans from the DSC experiment in the temperature range

up to 250 °C, indicating that the polymers are amorphous in the temperature range (Figure 4b).

3.4 Optical properties

The UV−vis absorption spectra of the two polymers **P1** and **P2** were recorded at room temperature both in dilute chloroform solution (ca. 10^{-6} M) and as thin films spin-coated onto quartz substrates (Figure 5). The detailed absorption data, including maximum absorbance (λ_{max}) in solution and solid state as well as the optical bandgaps, deduced from the absorption edge in films (E_g^{opt}), are summarized in Table 2. The UV spectrum of **P1** and **P2** polymers in chloroform exhibit a strong absorbance with λ_{max} at 700 nm and 710 nm, respectively. This absorption maximum of over 700 nm results from an intramolecular charge transfer (CT) state of the phenoxazine moieties alternate with diketopyrrolopyrrole moieties in the backbone.
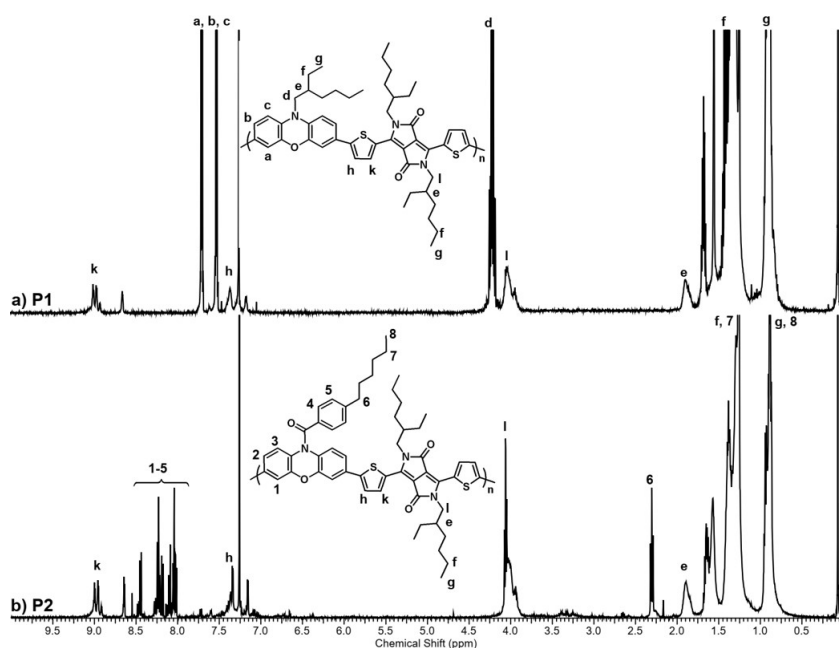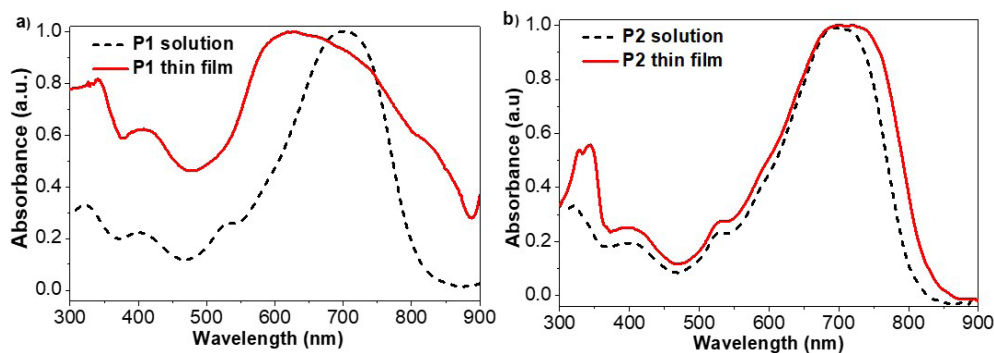

Figure 3. ^{1}H NMR spectra of **P1** (a) and **P2** (b) in CDCl$_3$.
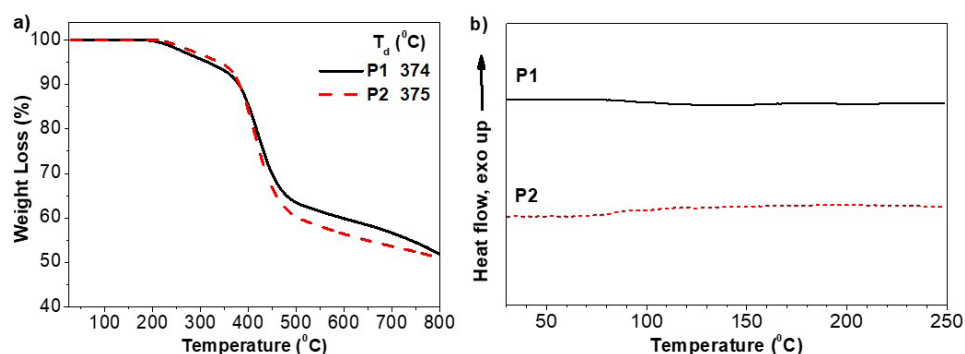
Figure 4. TGA (a) and DSC (b), second heating scans) curves of spectra of **P1** and **P2** with heating rate of 10 °Cmin^{-1} under nitrogen atmosphere. T_d represents the temperature of 10% weight loss.

Figure 5. UV–vis absorption spectra of P1 (a) and P2 (b) in CHCl₃ solution and thin film on a quartz substrate.

Table 2. Absorption maxima and energy levels of the polymers.

Polymer	λ_{max} solution (nm)	λ_{max} flim (nm)	$\lambda_{optical}$ film (nm)	$E_g^{optical}$ (eV)[a]
P1	700	628	850	1.46
P2	710	720	865	1.43

[a]Optical band gap estimated from the UV–vis absorption spectra edge in film, $E_g^{opt} = 1240/\lambda_{max\ onset}$. The solid-state UV-vis spectra were used to estimate the optical band gaps from the wavelength at the intersection of the tangent drawn at the low-energy side of the absorption spectrum with the x-axis.

The UV−vis spectra of thin films of all polymers show absorption throughout the visible region. Moreover, there is significant absorption extending into the near-IR region (as far as ca. 900 nm). In the thin film absorption spectrum, the 92 nm red shift in λ_{max} observed for the **P2** polymer compared to **P1** is due to the branched alkyl/benzoyl of group substitutions on phenoxazine. The optical band gaps for **P1** and **P2** polymers were calculated from the absorption cut off value in the solid state. In comparison, **P2** films exhibit slightly red-shifted absorption and a lower E_g^{opt} of 1.43 eV, whereas **P1** films exhibit blue-shifted absorption and a higher E_g^{opt} of 1.46 eV. The red-shifted absorption maxima in **P2** copolymer, indicating that the increased electronic delocalization arising from a more coplanar conformation and reduced steric interactions when benzoyl of group substitutions on phenoxazine moieties alternate with diketopyrrolopyrrole moieties in the backbone. The benzoyl system facilitates π-π interactions between copolymer chains, although the benzoyl substituent is not in direct but cross-conjugated conjugation with the polymer backbone[22]. The substitution of the branched alkyl side chain by a benzoyl ring system led to a significant red-shift of the absorption peak as well as a broadening of the absorption band both in solution and solid state.

4. Conclusions

In conclusion, two novel low-bandgap conjugated donor-acceptor copolymers based on phenoxazine with ethylhexyl/hexyl benzoyl side chain and diketopyrrolopyrrole were successfully synthesized by Pd-catalyzed direct arylation coupling polycondensation with high M_n (up to 41 500 g/mol) and high yield (>80%). Interestingly, the phenoxazine-based polymers with hexyl benzoyl side chains have higher molecular weights than those with branched ethylhexyl side chains. The benzoyl substitution also resulted in a broadening and redshift of the solid-state absorption spectra of the corresponding copolymer compared to the non-

benzoyl counterpart giving rise to lower optical bandgaps. These copolymers are promising candidate materials for developing new materials in optoelectronic applications.

5. Author's Contribution

- **Conceptualization** – Tam Huu Nguyen; Chau Duc Tran; Ha Tran Nguyen.

- **Data curation** – Thao Thanh Bui; Tam Huu Nguyen; Chau Duc Tran; Ha Tran Nguyen.

- **Formal analysis** – Tam Huu Nguyen; Bao Kim Doan; Le-Thu Thi Nguyen.

- **Funding acquisition** – Chau Duc Tran.

- **Investigation** – Tam Huu Nguyen; Thao Thanh Bui; Bao Kim Doan; Le-Thu Thi Nguyen.

- **Methodology** – Tam Huu Nguyen; Thao Thanh Bui; Bao Kim Doan; Le-Thu Thi Nguyen.

- **Project administration** – Chau Duc Tran.

- **Resources** – Tam Huu Nguyen; Chau Duc Tran.

- **Software** – Tam Huu Nguyen; Le-Thu Thi Nguyen.

- **Supervision** – Chau Duc Tran; Ha Tran Nguyen.

- **Validation** – Chau Duc Tran; Ha Tran Nguyen.

- **Visualization** – Tam Huu Nguyen; Chau Duc Tran; Ha Tran Nguyen.

- **Writing – original draft** – Tam Huu Nguyen; Chau Duc Tran; Ha Tran Nguyen.

- **Writing – review & editing** – Chau Duc Tran; Ha Tran Nguyen.

6. Acknowledgements

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