

Pd-catalysed oxidative C–H/C–H coupling polymerization for polythiazole-based derivatives



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ABSTRACT

Pd-catalysed oxidative C–H/C–H coupling homopolymerization of thiazole derivatives with different numbers ($n = 1–3$) of thiophene as bridged units was described. It represents a facile and practical methodology to prepare thiazole-based conjugated polymers in excellent yields. Three conjugated polythiazole derivatives (**P1–P3**) were synthesized by utilization of ligand-free Pd(OAc)₂ as a catalyst in the presence of Ag₂CO₃ and KOAc. Their chemical structure and molecular weights were established by ¹H and ¹³C NMR, as well as size exclusion chromatography (SEC), respectively. Polymerization conditions including amounts of Pd(OAc)₂ and oxidant, solvent medium and other catalysts were screened and optimized. Furthermore, the optical and electrical properties of the resulting polymers **P1–P3** were investigated by UV-vis and fluorescent spectroscopy, as well as cyclic voltammetry, respectively, and the influence of the length of bridged units on the photoelectric properties of these polymers was also discussed. This synthetic strategy would be applied in direct oxidative C–H/C–H coupling polymerization of other heteroarenes to construct versatile π -conjugated polymers for optoelectronic applications.

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1. Introduction

π -Conjugated polymers have gained much attention over the past few years primarily due to their solution processability and potential applications as active electronic elements for low-cost, large-area, and flexible active matrix display backplanes in organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs), organic field-effect transistors (OFETs) and optical sensors, etc. [1–6] Among them, thiazole-based conjugated polymers are of greater interest, which exhibit, in contrast to polythiophene analogues, lower-lying HOMOs and greater TFT air stability and larger current on–off ratios [7–9]. Conventionally, conjugated polythiazole derivatives are prepared through organometallic chemistry, which is limited for its long syntheses of the bifunctional aryl halides and/or organometallic monomers, a stoichiometric amount of toxic byproducts, and an extra end-capping

procedure for removal of terminal halogens or organometallic functional groups [7–9]. Recently, polycondensation via direct C–H arylation, which is widely recognized as an atom-economic and environmentally friendly method for synthesis of π -conjugated polymers in comparison to the traditional cross-coupling reactions, has also been achieved for the synthesis of conjugated polythiazole derivatives [10–12]. For examples, Kanbara's group reported a protocol via direct arylation of 4,4'-dinyonyl-2,2'-bithiazole with dibromoarylenes [13,14]. Although this protocol avoids the use of organometallic monomers, it still required multiple synthetic steps that sometimes are very challenging, and more importantly, end-capping procedures in most cases. Undoubtedly, the direct oxidative C–H/C–H coupling polymerization of nonpreactivated monomer would be one of the most ideal protocols for the synthesis of π -conjugated polymers. Recently, You and co-workers successfully developed an efficient method to prepare polybenzodiimidazoles via Cu-catalysed oxidative C–H/C–H coupling polymerisation [15]. But so far, direct C–H/C–H coupling polymerisation has been rarely reported for the synthesis of thiazole-based conjugated polymers.

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More recently, we developed a direct C–H/C–H coupling polymerization for efficient synthesis of polythiophene system [16]. It is necessary to broaden this methodology for polymerization of thiazole derivatives as new materials with many interesting optical and electrical properties. Since π -conjugated polymers containing thiazole units were reported to possess high potential as materials for OLED as well as PSCs, [7–9,17,18] synthesis of the polymers via direct C–H/C–H coupling will be very attractive for development of new semiconducting polymers. Herein, we report a new, simple and atom economical homopolymerization method through Pd-catalysed oxidative C–H/C–H coupling for preparation of a series of thiazole-based conjugated polymers containing thiophene units in the main chain, and their optical and electrical properties have been characterized.

2. Experimental section

2.1. Materials

All reactions and manipulations were carried out under argon atmosphere with the use of standard Schlenk techniques. 2,5-bis(trimethylstannyl)thiophene, 5,5'-bis(trimethylstannyl)-2,2'-bithiophene was bought from Zhongshen-huateng and all other starting organic compounds and organometallic compounds were purchased from Alfa Aesar, Aldrich, TCI and used without further purification. 2,5-bis(3-octyl-5-(tributylstannyl)thiophen-2-yl)thiophene were prepared according to procedures reported in the literature [19]. All the monomers were carefully purified prior to use in the polymerization reaction.

2.2. Measurements

^1H and ^{13}C NMR spectra were recorded on a Bruker AV400 using residual solvent peak as a reference. High-resolution matrix-assisted laser desorption ionization (MALDI) mass spectra were collected with a Fourier transform-ion cyclotron resonance mass spectrometer instrument (Varian 7.0T FTICR-MS). Number-average (M_n) and Weight-average (M_w) molecular weights were determined by size exclusion chromatography (SEC) in tetrahydrofuran at 25 °C using Waters 1525 with Waters Styragel HT gel columns. For the calibration curve, a series of monodisperse polystyrene standards (Shodex) was used. Thermogravimetric analyses (TGA) were carried out on a Netzsch TG209 instrument under a purified nitrogen gas flow with a 10 °C min⁻¹ heating rate. UV-vis-NIR absorption spectra were recorded using a shiftmadzu UV-2550 and spin cast films on glass plates were used for the solid-state measurements. Optical bandgaps were determined from the onset of the absorption band. Cyclic voltammetry (CV) experiments were performed with a LK98B II microcomputer-based electrochemical analyzer. All CV measurements were carried out at room temperature with a conventional three-electrode configuration using a glassy carbon electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a Pt wire as the counter electrode. Acetonitrile was distilled from calcium hydride under dry nitrogen immediately prior to use. Tetrabutylammonium phosphorus hexafluoride (Bu_4NPF_6 , 0.1 M) in acetonitrile was used as the support electrolyte, and the scan rate was 100 mV s⁻¹. X-ray diffraction (XRD) experiments were performed on a Bruker D8 FOCUS X-ray diffractometer with Cu K α radiation ($k = 1.5406 \text{ \AA}$) at a generator voltage of 40 KV and a current of 40 mA.

2.3. Synthesis

2.3.1. Synthesis of dodecyl 2-bromothiazole-4-carboxylate

A solution of dodecyl alcohol (1.19 g, 6.38 mmol) and 2-bromothiazole-4-carboxylic acid (1.60 g, 7.69 mmol) in 30 mL

chloroform was added 4-dimethylaminopyridine (738 mg, 6.01 mmol). After stirring for 1 h, N,N'-carbonyldiimidazole (834 mg, 5.14 mmol) were added. The reaction mixture was stirred for 9 h, the solvent was removed in *vacuo* and the residue purified by flash chromatography (2 × 20 cm, petroleum ether/ethyl acetate = 7/1) to yield 1.72 g (4.57 mmol, yield 71.6%) of dodecyl 2-bromothiazole-4-carboxylate as pale white solid. ^1H NMR (400 MHz, CDCl_3) δ : 8.10 (s, 1H), 4.35 (t, 2H, $-\text{OCH}_2-$), 1.82–1.72 (m, 2H), 1.46–1.19 (m, 20H), 0.88 (t, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ : 160.03 (s), 147.32 (s), 136.62 (s), 130.76 (s), 65.86 (s), 31.88 (s), 29.74–29.07 (m), 28.63 (s), 25.85 (s), 22.65 (s), 14.08 (s). MS (MALDI-TOF): calcd. for $\text{C}_{16}\text{H}_{26}\text{BrNO}_2\text{S}$ $[\text{M}+\text{H}]^+$, 375.09; found, 376.08.

2.3.2. Synthesis of M1

A solution of dodecyl 2-bromothiazole-4-carboxylate (120 mg, 0.318 mmol) and 2,5-bis(trimethylstannyl)thiophene (62.20 mg, 0.152 mmol) in toluene (15 mL) was degassed twice with argon followed by the addition of $\text{Pd}(\text{PPh}_3)_4$ (18 mg, 0.015 mmol). After being stirred at 115 °C for 10 h under argon, the reaction mixture was poured into water (100 mL) and extracted with CH_2Cl_2 . The organic layer was washed with water and then dried over Na_2SO_4 . After removal of solvent, the crude product was purified by column chromatography on silica gel using a mixture of dichloromethane and petroleum ether (2:1) as eluant to afford compound (81.68 mg, 0.121 mmol, yield 79.6%) as a red solid. ^1H NMR (400 MHz, CDCl_3) δ : 8.14 (s, 2H), 7.61 (s, 2H), 4.39 (t, 4H, $-\text{OCH}_2-$), 1.88–1.76 (m, 4H), 1.43–1.19 (m, 37H), 0.90 (t, $J = 6.8 \text{ Hz}$, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ : 160.13 (d), 147.12 (s), 137.54 (s), 126.86 (s), 125.89 (s), 64.78 (s), 30.90 (s), 28.87–27.95 (m), 27.64 (s), 24.91 (s), 21.67 (s), 13.11 (s). MS (MALDI-TOF): calcd. for $\text{C}_{36}\text{H}_{54}\text{N}_2\text{O}_4\text{S}_3$ $[\text{M}+\text{H}]^+$, 674.32; found, 675.33.

2.3.3. Synthesis of M2

The preparation process refer to the process of M1, the crude product was purified by column chromatography on silica gel using a mixture of dichloromethane and petroleum ether (2:1) as eluant to afford compound (99.18 mg, 0.131 mmol, yield 90.3%) as a red solid. ^1H NMR (400 MHz, CDCl_3) δ : 8.08 (s, 2H), 7.50 (d, $J = 3.9 \text{ Hz}$, 2H), 7.22 (d, $J = 3.9 \text{ Hz}$, 2H), 4.37 (t, 4H, $-\text{OCH}_2-$), 1.84–1.76 (m, 4H), 1.44–1.24 (m, 36H), 0.88 (t, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ : 169.45–162.61 (m), 161.37 (d), 147.90 (s), 145.28–140.85 (m), 137.59 (d), 128.36 (s), 126.42 (s), 125.13 (s), 65.76 (s), 31.93 (s), 29.91–29.13 (m), 28.68 (s), 25.94 (s), 22.71 (s), 14.14 (s). MS (MALDI-TOF): calcd. for $\text{C}_{40}\text{H}_{56}\text{N}_2\text{O}_4\text{S}_4$ $[\text{M}+\text{H}]^+$, 756.31; found, 757.30.

2.3.4. Synthesis of M3

The preparation process refer to the process of M1, the crude product was purified by column chromatography on silica gel using a mixture of dichloromethane and petroleum ether (2:1) as eluant to afford compound (165.94 mg, 0.156 mmol, yield 86.1%) as a red solid. ^1H NMR (400 MHz, CDCl_3) δ : 8.05 (s, 2H), 7.45 (s, 2H), 7.17 (s, 2H), 4.36 (t, 4H, $-\text{OCH}_2-$), 2.80 (t, 4H), 1.84–1.75 (m, 4H), 1.69 (dd, 4H), 1.44–1.25 (m, 56H), 0.88 (t, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ : 160.87 (s), 160.20 (s), 146.94 (s), 139.58 (s), 135.00 (s), 132.74 (s), 129.41 (s), 125.84 (s), 125.07 (s), 64.67 (s), 30.89 (d), 29.47 (s), 28.45 (ddd), 27.69 (s), 24.94 (s), 21.66 (d), 13.07 (s). MS (MALDI-TOF): calcd. for $\text{C}_{60}\text{H}_{90}\text{N}_2\text{O}_4\text{S}_5$ $[\text{M}+\text{H}]^+$, 1062.55; found, 1063.53.

2.3.5. General procedure for synthesis of polymers

To a 25 mL round bottom flask with a reflux condenser were added monomer (1 equiv), Ag_2CO_3 (2.0 equiv), Potassium Acetate (2.0 equiv) and DMAc (4 mL). The mixture was stirred at 110 °C for 10 min, then was degassed twice with argon followed by addition of palladium acetate as a catalyst (5 mol %) dissolved in 1 mL of DMAc

to the reaction flask. After stirring at 110 °C for 72 h under argon, the mixture was cooled to room temperature and poured in 100 mL of cold methanol. The precipitate was filtered out as the crude product. Soxhlet extraction with methanol was applied to remove the catalyst and this was followed by hexanes extraction to remove the low-molecular-weight materials. The final polymer was isolated as a solid and dried under vacuum at 60 °C over a period of 12 h.

P1: Following the general polymerization procedure, **M1** (150 mg, 0.222 mmol), Ag₂CO₃ (122.54 mg, 0.444 mmol), KOAc (43.62 mg, 0.444 mmol) were used for the polymerization; yield = 97%; M_n = 6 kDa, PDI = 1.46. ¹H NMR (400 MHz, CDCl₃) δ: 7.60 (d, 2H), 4.22 (s, 4H, -OCH₂-), 1.62 (br, 4H), 1.42–1.10 (m, 36H), 0.88 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ: 164.27 (s), 132.75 (s), 128.72 (s), 61.73 (s), 31.01–27.72 (m), 28.34–27.72 (m), 21.68 (s), 13.11 (s).

P2: Following the general polymerization procedure, **M2** (300 mg, 0.396 mmol), Ag₂CO₃ (218 mg, 0.792 mmol), KOAc (78 mg, 0.792 mmol) were used for the polymerization; yield = 96%; M_n = 8 kDa, PDI = 2.11. ¹H NMR (400 MHz, CDCl₃) δ: 7.54 (d, 2H), 4.14 (t, 4H, -OCH₂-), 1.88 (s, 4H), 1.28–0.88 (m, 58H), 0.88 (m, 12H).

P3: Following the general polymerization procedure, **M3** (300 mg, 0.282 mmol), Ag₂CO₃ (155 mg, 0.564 mmol), KOAc (55 mg, 0.564 mmol) were used for the polymerization; yield = 98%; M_n = 13 kDa, PDI = 1.22. ¹H NMR (400 MHz, CDCl₃) δ: 7.47 (s, 2H), 7.23 (s, 2H), 4.23 (t, -OCH₂-, 4H), 2.84 (s, 4H), 1.73 (s, 4H), 1.58 (s, 4H), 1.40–1.20 (m, 60H), 0.91–0.86 (m, 12H). ¹³C NMR (100 MHz, CDCl₃) δ: 161.57 (s), 161.02 (s), 145.16 (s), 140.73 (s), 136.03 (s), 134.47 (s), 133.02 (d), 130.92 (d), 129.74 (s), 126.98 (s), 65.95 (s), 31.91 (d), 30.48 (s), 29.80–29.12 (m), 28.49 (s), 25.98 (s), 22.69 (s).

3. Results and discussion

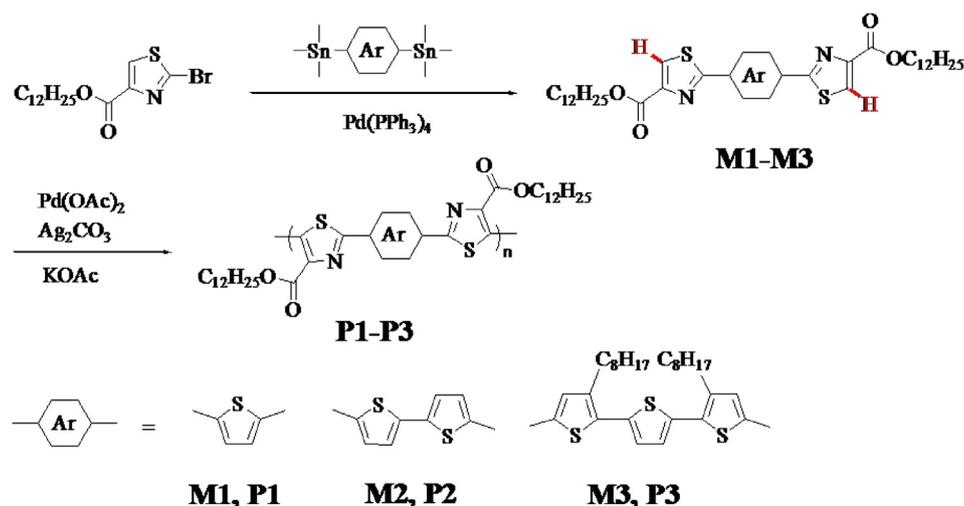
3.1. Design and synthesis

Three copolymers **P1–P3** were synthesized by Pd-catalysed oxidative C–H/C–H coupling reactions using ligand-free Pd(OAc)₂ as a catalyst and in the presence of Ag₂CO₃ and KOAc under mild conditions as shown in Scheme 1. The three kinds of monomers with different numbers (n = 1–3) of thiophene as bridged units were used to inspect that C–H bond is alive to prepare C–C bond when the conjugated chain is extended. The **M3** with long alkyl side-group on thiophene ring increased solubility of monomer as

well as the corresponding polymer with a high polymerization degree. Otherwise, the polythiazole with three thiophenes in absence of alkyl groups would precipitate from the polymerization system. In such a case, the polymerization would cease to obtain polythiazoles with smaller molecular weight than that with alkyl groups [13,14,20]. We began our investigation using **M3** as the model substrate for screening and optimizing conditions for Pd-catalysed oxidative C–H/C–H coupling polymerization, considering its better solubility in common organic solvents compared to **M1** and **M2** due to the long chain alkyl groups attached to the thiophene ring. The results were summarized in Table 1.

In order to study the influence of quantity of catalyst on the reaction, the polymerization for **P3** was first performed under N₂ in N,N-dimethylacetamide (DMAc) in the presence of Ag₂CO₃, KOAc and various amounts of Pd(OAc)₂. Ligand-free Pd(OAc)₂ was found to efficiently catalyse the direct C–H/C–H coupling homopolymerization of thiazole derivatives even employing as little as 0.01% catalyst concentration (Entry 3). Moreover, increasing the amount of Pd(OAc)₂–5 % (mol %) led to a higher yield of 98% with a M_n of 13 000 (PDI of 1.22) (Entry 5). Reducing the loading of Ag₂CO₃ only afforded a decreased yield (down 10–25 %) and M_n (Only half of the original M_n, 6–7 kDa) (Entry 8 and 9). To our expectations, the palladium catalysed cyclic process may not experience zero valent palladium process. As the article mentioned, [16] Pd(0) may be reduced from Pd(II) by either the ligand as reductant or the active hydrogen atom on the aromatic ring [10]. This would be our next focus of study. In the previous work, we used copper carbonate asco-catalyst, in view of thiazole containing nitrogen atom, while copper cation may form complex with thiazole ring to reduce its catalytic effect [16,21–25]. Anyhow, Cu(OAc)₂ as a co-catalyst also afford a moderate yield (86%, M_n = 8 kDa, PDI = 2.37) in the present work (Entry 11). When the carbonate ligand (Entry 5) in co-catalyst was replaced by fluorine anion (Entry 10), the yield and molecular weight of the resultant polymer decreased (81%, M_n = 7 kDa), which showed that the reaction required basic of carbonate. The yield of the resultant polythiazole dropped to 83%, molecular weight was also low (M_n = 8 kDa, PDI = 1.28), while the reaction was carried out in absence of potassium acetate (Entry 12). As mentioned previous work, the acetate was not only as ligand, but also as one of buffer [16].

Among the solvents screened, DMAc (Entry 5) was proved to be more efficient for polymerization than the other solvents. A narrow distribution of **P3** was achieved using high polar aprotic solvents



Scheme 1. Synthesis of polymers **P1–P3** through Pd-catalysed oxidative direct C–H/C–H coupling.

Table 1
The screening of the reaction conditions for the polymerization of **P3** by Pd-catalysed oxidative C–H/C–H coupling.^a

Entry	Catalyst	Quantity of catalyst (mol %)	Oxidant	Solvent	Additive	Yield ^b	M_n	PDI
1	Pd(OAc) ₂	1%	Ag ₂ CO ₃	DMAc	KOAc	85	8	2.13
2	Pd(OAc) ₂	0.1%	Ag ₂ CO ₃	DMAc	KOAc	86	8	2.14
3	Pd(OAc) ₂	0.01%	Ag ₂ CO ₃	DMAc	KOAc	84	7	2.04
4	Pd(OAc) ₂	0%	Ag ₂ CO ₃	DMAc	KOAc	–	–	–
5	Pd(OAc) ₂	5%	Ag ₂ CO ₃	DMAc	KOAc	98	13	1.22
6	Pd(OAc) ₂	5%	Ag ₂ CO ₃	NMP	KOAc	82	9	2.05
7	Pd(OAc) ₂	5%	Ag ₂ CO ₃	DMSO	KOAc	78	6	1.46
8	Pd(OAc) ₂	5%	–	DMAc	KOAc	85	7	2.01
9	Pd(OAc) ₂	5%	–	DMAc	K ₂ CO ₃	74	6	1.14
10	Pd(OAc) ₂	5%	AgNO ₃ /NaF ^c	DMAc	KOAc	81	7	1.48
11	Pd(OAc) ₂	5%	Cu(OAc) ₂	DMAc	K ₂ CO ₃	86	8	1.28
12	Pd(OAc) ₂	5%	Ag ₂ CO ₃	DMAc	–	83	8	2.37
13	Pd(OAc) ₂	0%	FeCl ₃ ^d	CHCl ₃	–	–	–	–
14	PdCl ₂	5%	Ag ₂ CO ₃	DMAc	KOAc	83	10	1.70
15	Pd(PPh ₃) ₄	5%	Ag ₂ CO ₃	NMP	KOAc	53	4	1.12
16	Pd(PPh ₃) ₄	5%	Ag ₂ CO ₃	DMAc	KOAc	84	12	2.28
17	Pd(PPh ₃) ₄	5%	–	DMAc	KOAc	67	8	1.45
18	Pd(PPh ₃) ₄	5%	–	DMAc	K ₂ CO ₃	31	3	1.05
19	Pd(PhCN) ₂ Cl ₂	5%	Ag ₂ CO ₃	DMAc	KOAc	82	12	1.16
20	Pd(dppf)Cl ₂	5%	Ag ₂ CO ₃	DMAc	KOAc	81	10	1.24

^a Reaction conditions: substrate (1 equiv), oxidant (2.0 equiv), additive (2.0 equiv) in 5 mL of DMAc at 110 °C in N₂ for 72 h.

^b The products were obtained by reprecipitation from CHCl₃–CH₃OH.

^c NaF/AgNO₃ = 1:2.1.

^d FeCl₃ (6 equiv).

(e.g. DMSO and NMP) at the cost of decreased yields and M_n (Table 1, Entries 5–7).

Other palladium catalysts, such as PdCl₂, Pd(PPh₃)₄, Pd(PhCN)₂Cl₂ and Pd(dppf)Cl₂ could also be used for the synthesis, Zero valent palladium reagent Pd(PPh₃)₄ also received a good yield and molecular weight, this prompted us to further thinking of palladium valence state of the catalytic process (Table 1, Entries 14–20). Further, it was noted that the traditional oxidant FeCl₃ (Entry 13) was not compatible for the polymerization of substrate, which may be related to the deficient electron at the 5-position of the substrate because of the electron-withdrawing ester groups directly attached to the thiazole ring [26]. As a result, this directly efficient Pd-catalysed oxidative C–H/C–H coupling polymerization promises to be an exceedingly general method for the synthesis of a large variety of polythiazole containing electron-withdrawing groups.

According to the optimized polymerization conditions for **P3**, **P1** and **P2** were also synthesized and various properties of these polymers are given in Table 2. The chemical structures of these polymers were identified by ¹H and ¹³C NMR spectra, and their ¹H NMR spectra were presented in Fig. 1. In the NMR spectra, all signals could be assigned to protons in the repeating units. Only weak signal of the terminal units was observed, which well agreed to the resultant polythiazoles with moderate molecular weight (M_n = 6–13 kDa) as demonstrated by SEC. In addition, the absolute molecular weights of these polymers were also estimated by

Table 2
Characterization of polymers **P1–P3**.

Entry	Yield (%) ^a	M_n (kDa) ^b	M_w (kDa) ^b	PDI ^b	M^c	T_d (°C) ^d
P1	97	6	8	1.46	5.4	324
P2	96	8	17	2.11	4.6	346
P3	98	13	16	1.22	8.5	371

^a Insoluble in methanol.

^b Estimated by SEC measurements (eluent: THF, standard: polystyrene). M_n = Number-average molecular weight, M_w = Weight-average molecular weight, PDI = Polydispersity index.

^c Molecular weight estimated by the integration ratio of peak area of the proton signals from the –OCH₂ relative to that of the proton signals from the end proton.

^d Decomposition temperature taken as the temperature corresponding to a 5% weight loss in the thermogravimetric run (10 °C/min, N₂).

determining the integration ratio of peak area of the proton signals from the –OCH₂ with chemical shift at 4.3 ppm relative to that of the proton signals from the end proton with chemical shift at 8.1 ppm and the data were shown in Table 2. Due to the slight solubility of the resulting polymers in common solvents, such as CHCl₃, THF, DMSO, DMF and so on, it is very difficult to obtain the really average molecular weight of the total polymers. For clarity, it should be noticed that the SEC and NMR data were determined from the solvable polythiazole samples in THF and chloroform. It is very difficult to get the detail data for those not soluble in these solvents, which may have higher molecular weight with too limited solubility.

The thermal stabilities of the polymers were evaluated by thermogravimetric analysis (TGA, Fig. S11). TGA of the polymers showed the onset temperatures of decomposition at about 310 °C, and there were about 5% weight loss by 324, 346 and 371 °C for **P1**, **P2** and **P3**, respectively, showing good thermally stable under N₂. These data suggest that the conjugated polymers synthesized by the direct C–H/C–H coupling polymerization are stable enough for optoelectronic applications.

3.2. X-ray diffraction studies

To evaluate the crystallinity of polymers **P1–P3**, XRD measurements were taken of thick drop cast films that were annealed at 120 °C. As shown in Fig. 2 and Fig. S12, only **P2** exhibited distinct diffraction peak at $2\theta = 2.27^\circ$, corresponding to an interchain lamellar d-spacing of 38 Å. The far interchain distance for **P2** as well as almost negligible diffraction peak for **P1** and **P3** should be related to ester groups directly attached to the thiazole ring, which probably force the backbone to adopt a nonplanar orientation in the film state.

3.3. Optical properties

UV-vis absorption spectra of polymers **P1–P3** in dilute chloroform solution and as spin-coated films were displayed in Fig. 3 and the data are summarized in Table 3. **P1–P3** exhibited broad absorption in the range 300–500 nm with maximum absorption

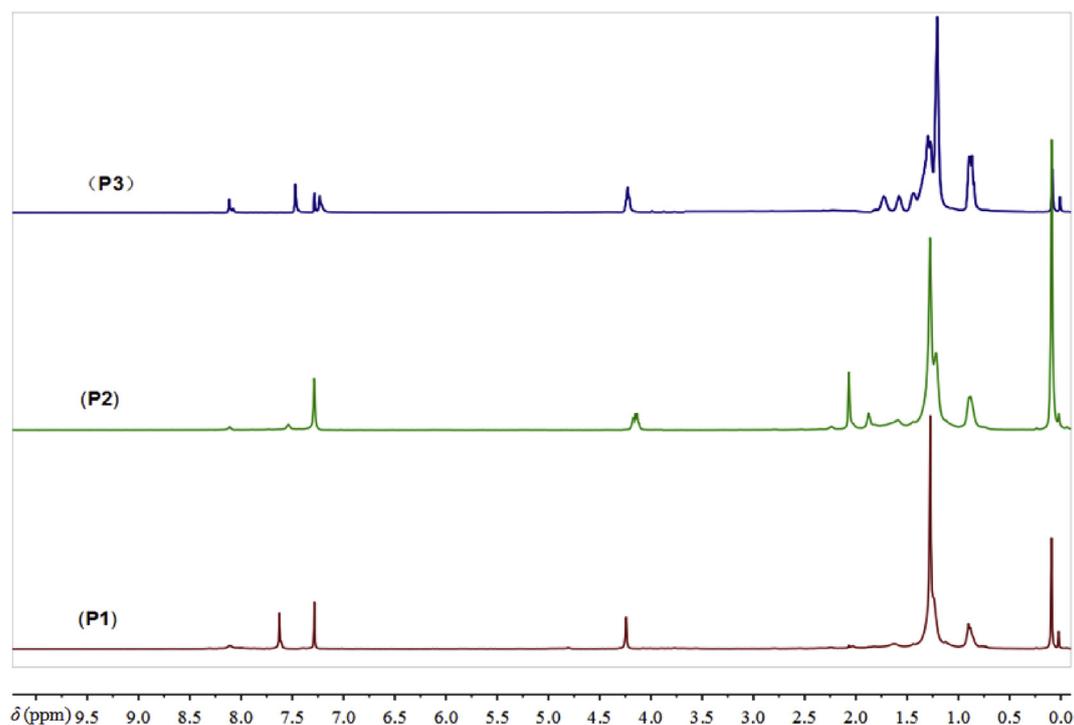


Fig. 1. ^1H NMR spectra of **P1–P3**.

peaks at 394, 430 and 443 nm in the solution state, respectively. With the increasing numbers of bridged thiophene units, the absorption maximum is gradually red-shifted, which indicates more significant planarization of the polymer main chain (highly conjugated) with the increase in the thiophene moieties. In the film state, similar to other π -conjugated polymers, UV-vis absorption peaks of polymers **P1** and **P3** are shifted to longer wavelengths (red-shift) relative to those measured in solution. This behaviour is due to the intermolecular interactions between the polymer chains and the planarization effect of the π -conjugated polymer backbone, which enable the polymer chains to self-assemble into a well-ordered nanostructure in the solid state (J-type aggregates) [27–29]. As shown in Fig. 3b, **P1** and **P3** were characterized by the main absorption bands with λ_{max} at 420 and 505 nm with red-shifts of 26 and 62 nm compared to those in solution state, respectively, which

suggests **P3** with longer thiophene segments is easier to form ordered aggregation in solid state than **P1**. Moreover, the vibronic features were resolved in **P2** with a maximum absorption band at 364 nm and a shoulder peak at 443 nm in the film state, which is probably related to H-type and J-type aggregates, respectively [27–29]. The results are consistent with those of XRD of **P2**.

Fluorescence spectra of the polymers in the solution and film states are also examined and shown in Fig. 4. As shown in Fig. 4a, **P2** exhibits fine structure in the emission spectra in the solution state, which suggests that the polymer **P2** are likely to be aggregated mainly as H-type aggregates characterized by blue-shift of emission peaks even in the dilute solution. To further confirm the aggregation of **P2** in the solution, the influence of polymer **P2** concentration on the fluorescence spectra was investigated. As shown in Fig. 5, fluorescent intensities decrease gradually with the increase of polymer solution concentration, which is attributed to more efficient radiationless decay in the ordered phase. The fluorescent intensity in the film state was extremely weak compared with that in the solution state as shown in Fig. 4b. Emission maxima were observed at 609, 626, 645 nm, for **P1**, **P2** and **P3** in the film state, respectively. As in the case of absorption maximum in the solution, the emission maximum in film state also red-shifted with increase in the thiophene moieties.

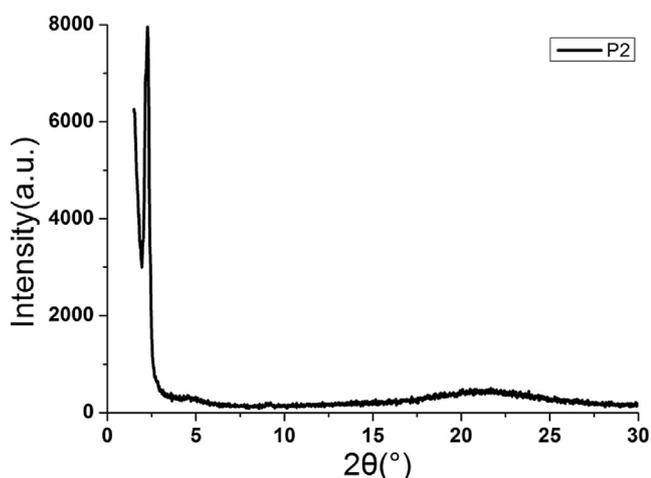


Fig. 2. Thin film X-ray diffraction profiles of **P2**.

3.4. Electrical properties

The electrochemical properties of the polymer films cast from CHCl_3 were measured using cyclic voltammetry with ferrocene/ferroceniums the standard. Fig. S13 shows the cyclic voltammograms of **P1–P3** on a glassy carbon electrode in the presence of 0.1 mol L^{-1} Bu_4NPF_6 acetonitrile solution as an electrolyte. The energy corresponding to the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) was calculated from the corresponding cyclic voltammograms. All three polymers exhibited both oxidation (*p*-doping) due to the electron

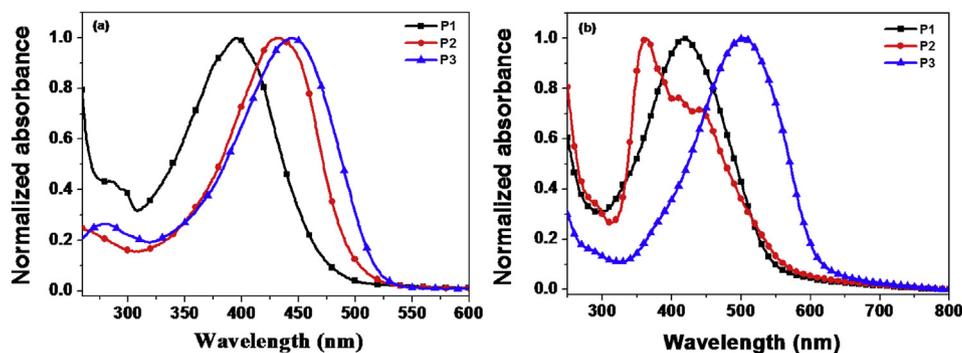


Fig. 3. Normalized absorption spectra of **P1–P3** (a) in dilute chloroform solution and (b) in the thin film state (spin-cast from chloroform solution).

Table 3
Optical properties of **P1–P3**.

Entry	λ_{\max} (nm) ^[a]	λ_{\max} (nm) ^[b]	λ_{PL} (nm) ^[c]	λ_{PL} (nm) ^[d]	λ_{onset} (nm) ^[e]	$E_{\text{g}}^{\text{opt}}$ (eV) ^[f]
P1	394	420	526	609	554	2.24
P2	430	364, 443	456, 481, 518	626	575	2.16
P3	443	505	570	645	619	2.00

^[a] and ^[b] from the UV-Vis absorption spectra in solution and film, respectively.

^[c] and ^[d] from the fluorescence spectra in solution and film, respectively.

^[e] the onset absorption of the thin film.

^[f] Estimated from the onset absorption of the thin film.

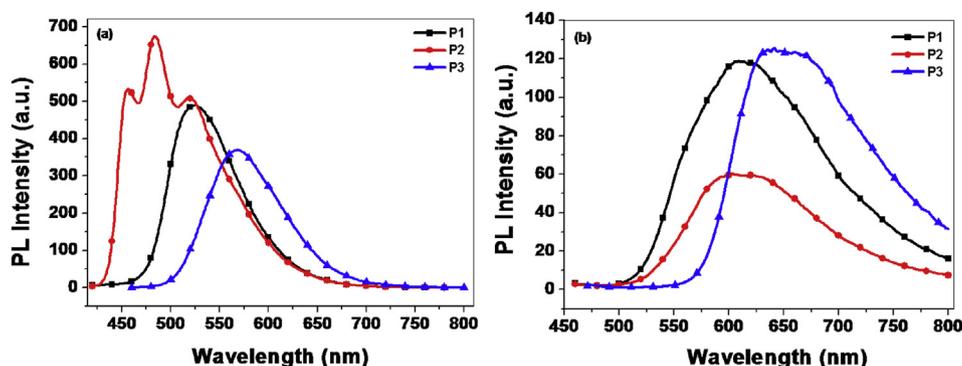


Fig. 4. Fluorescence spectra of **P1–P3** (a) in chloroform solution (λ_{ex} = 400 nm for **P1**, **P2**, and 440 nm for **P3**) (b) in the thin film state (spin-cast from chloroform solution, λ_{ex} = 440 nm for **P1**, **P2**, and 450 nm for **P3**).

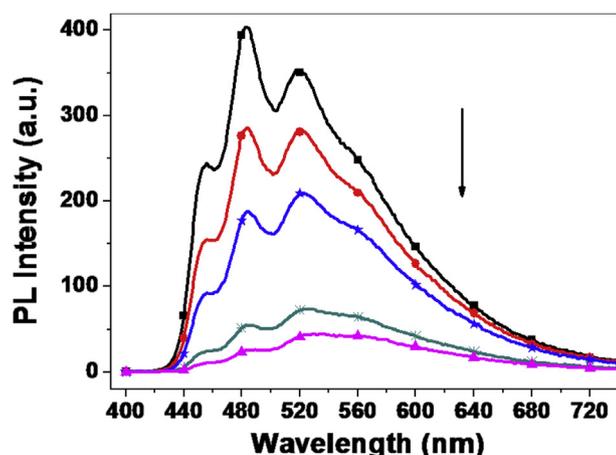


Fig. 5. Effect of polymer **P2** concentrations in CHCl_3 solution on their fluorescence spectra, $[\text{P2}] = 60, 80, 100, 120, 150 \mu\text{M}$, $\lambda_{\text{ex}} = 380 \text{ nm}$.

rich thiophene moieties and reduction (*n*-doping) due to the electron deficient thiazole moieties. Oxidation was found to be reversible for **P2** and partially reversible for **P1** and **P3**, whereas reduction was found to be reversible in all three polymers. The HOMO and LUMO energy levels of the polymers were calculated according to the following equations:

$$\text{HOMO} = -e(E_{\text{onset}}^{\text{ox}} + 4.8) (\text{eV})$$

$$\text{LUMO} = -e(E_{\text{onset}}^{\text{red}} + 4.8) (\text{eV})$$

where E_{ox} and E_{red} are oxidation and reduction potentials respectively. They were obtained from the onset of the corresponding potentials in the cyclic voltammograms. The onset oxidation potentials were found to be at 1.13 V, 1.08 V and 0.82 V for **P1–P3**, respectively versus Fc/Fc^+ , which correspond to the HOMO energy levels of -5.92 , -5.87 and -5.61 eV. Similarly, the onset reduction potentials were found to be at 1.64 V, 1.70 V and 1.79 V for **P1–P3**, respectively versus Fc/Fc^+ , which correspond to the LUMO energy

Table 4
Electrochemical properties of **P1–P3**.

	P1	P2	P3	M1	M2	M3
E_{HOMO} (eV)	−5.92	−5.87	−5.61	−6.01	−6.37	−5.48
E_{LUMO} (eV)	−3.15	−3.09	−3.00	−2.90	−2.73	−2.77
E_{g}^{CV} (eV)	2.77	2.78	2.61	3.11	3.64	2.71

levels of −3.15, −3.09 and −3.00 eV. The energy level diagrams are shown in Fig. S13. The electrochemical band gaps were calculated to be 2.77 eV, 2.78 eV and 2.61 eV respectively for **P1–P3**. By extrapolation of the absorption onsets in the film state, the optical band gaps were estimated to be 2.53, 2.45 and 2.37 eV for **P1**, **P2** and **P3**, respectively. The values measured by cyclic voltammetry (CV) were higher when compared to the band gap calculated from the absorption spectrum (Table 3, Fig. S13), indicate increasing the bridged thiophene units will lower the optical band gap of polymers. All the electrochemical parameters are given in Table 4.

4. Conclusions

In conclusion, we have developed an efficient method to prepare polythiazole-based π -conjugated polymer via Pd-catalysed oxidative C–H/C–H coupling polymerization for the first time, which maybe serve as a general, simple and efficient methodology to access this kind of important materials. In comparison to the conventional cross-coupling reactions, our new protocol proceeded smoothly with a significantly reduced catalyst loading (0.01 mol %) and without a sacrifice in yield. Our new methodology is also environmentally friendly and avoids many issues by using the conventional organometallic intermediates. We expect that this efficient strategy would be applied in direct oxidative C–H/C–H coupling polymerization of other heteroarenes to construct versatile π -conjugated polymers for optoelectronic applications.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.polymer.2015.05.035>.

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