The synthesis of 5-alkyl[3,4-c]thienopyrrole-4,6-dione-based polymers using a Pd-catalyzed oxidative C–H/C–H homopolymerization reaction†

Qiang Zhang,[a] Xiangjian Wan,[a] Yan Lu,*[b] Yandong Li,[a] Yuefeng Li,[a] Chenxi Li,*[a] Hao Wu[a] and Yongsheng Chen*[a]

A new, simple, mild, atom economical homopolymerization method through Pd-catalyzed oxidative C–H/C–H coupling was developed for the preparation of a series of 5-alkyl[3,4-c]thienopyrrole-4,6-dione-based conjugated polymers.

Direct C–H/C–H coupling is obviously the best and most economical way to build new C–C bonds for the synthesis of new materials, with many advantages, such as being more atom economical, possessing more diverse starting materials and avoiding the issue of end-capping groups.[1] Indeed, there have been some reports of using this approach to prepare small molecules,[1a,b,e] for example, bisthiophene systems.[2] For the synthesis of polymers, homopolymerization and copolymerization of various aromatic systems have widely employed the corresponding Ar-halides and organometallic intermediates, generally using Pd(O) as the catalyst.[3] For example, transition metal-catalyzed coupling reactions including Suzuki–Miyaura, Negishi, Kumada, Heck and Stille reactions have been widely used for synthesizing conjugated polymers in an efficient manner, especially for those with intramolecular donor–acceptor structures.[3,4] However, pre-activated monomers with metal-containing functionalities and halides are generally necessary for these conventional coupling reactions, which need multiple synthesis steps and sometimes suffer from difficult synthesis procedures and/or instability of the corresponding organometallic intermediates, and in many cases, the toxicity of monomers with metal-containing functionalities is another big issue. In addition, end-capping procedures have to be carried out in most cases because the terminal halide

or metal-containing functionalities are detrimental to the intrinsic properties of the corresponding polymer-based devices.[3c,5]

Big advances come from the recent studies, which have reported a heteroarylation method by direct carbon–carbon bond formation to synthesize some small molecules and copolymers.[3c,5,6] Though direct C–H/C–H coupling has been investigated widely for many small molecule systems, in most cases relatively activated C–H bonds are needed to achieve the direct C–C coupling and the choice of substrates is rather limited.[7] The question then is whether we can use it for general polymerization without using the corresponding monomer halides to shorten the whole synthesis procedure, because in many cases it is hard to obtain the intermediates. This is especially greatly required for many functional photoelectronic polymers. Indeed, in our pursuit of organic/polymeric photovoltaic materials,[8] a challenge often facing us is the achievement of direct C–C coupling without synthesizing such aromatic halides and/or their organometallic compounds. This could offer many advantages particularly when complicated systems with multifunctional groups exist. And indeed, to the best of our knowledge, no such work on the Pd-catalyzed oxidative C–H/C–H coupling reaction has been reported for polymer synthesis. In this work, we wish to report such a Pd-catalyzed oxidative C–H/C–H coupling reaction to synthesize new small molecules and the corresponding conjugated polymers (Scheme 1), in which thieno[3,4-c]pyrrole-4,6-dione (TPD), dithieno-silole (DTS) and benzo[1,2-b:4,5-b′]dithiophene (BDT) based units, widely used as efficient building blocks for organic solar cells (OSCs), are employed as the reaction aromatic units.

As shown in Scheme 1, three series of polymers **P1–P3** were synthesized using Pd-catalyzed oxidative C–H/C–H coupling reactions with Pd(OAc)$_2$ as the catalyst in the presence of Cu(OAc)$_2$ and K$_2$CO$_3$ under mild conditions. The detailed synthesis procedures are presented in the ESI.† Table 1 summarizes the optimized polymerization results for the molecular weight and polydispersity index (PDI) of the three polymers. We were pleasantly surprised to see that the Pd-catalyzed oxidative coupling reaction works well for polymers **P1–P3**. The polymer products are confirmed by their NMR, size exclusion

[a] Key Laboratory of Functional Polymer Materials, Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Center for Nanoscale Science and Technology, Institute of Polymer Chemistry, College of Chemistry, Nankai University, Tianjin, 300071, China. E-mail: yschen99@nankai.edu.cn, lichenxi@nankai.edu.cn

[b] School of Materials Science & Engineering, Tianjin University of Technology, Tianjin, 300384, China. E-mail: luyan@tjut.edu.cn

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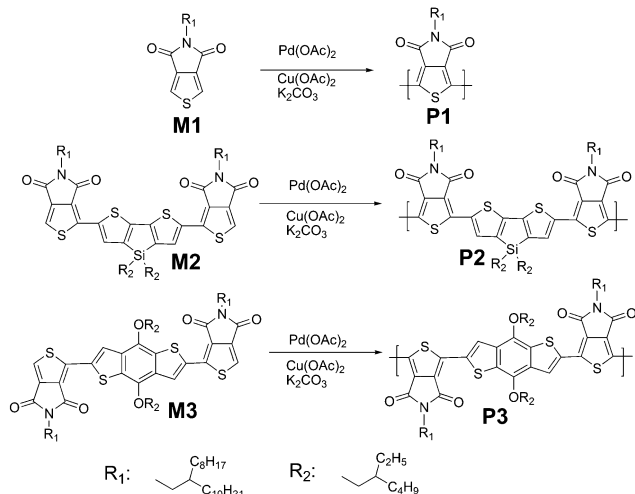
Scheme 1 Synthesis of polymers **P1**–**P3** through Pd-catalyzed oxidative direct C–H/C–H coupling.

Table 1 Characterization of polymers **P1**–**P3**[a]

Polymer	Yield (%)	M_n (kDa)	M_w (kDa)	PDI
P1	96	4	7	1.75
P2	86	16	22	1.37
P3	88	18	23	1.28

[a] Isolated yield after purification. M_n = number-average molecular weight, M_w = weight-average molecular weight, PDI = polydispersity index.

chromatography (SEC) and thermogravimetric analysis (TGA) (see the ESI† for details).

As shown in Table 1, **P1**–**P3** could be produced with high yields with a molecular weight of up to tens of thousands. Furthermore, it is important to note that the above polymerized products (for example, **P3'** with $M_n \sim 7$ kDa) could then be used as the starting materials to perform the same polymerization under the same conditions after adding a new catalyst to achieve even higher polymerization degrees (**P3''** with $M_n \sim 23$ kDa) (see the polymerization procedure of **P3''** in the ESI† for details), which allows a controlled molecular weight to be achieved.

The monomer **M3** was chosen as the reaction substrate for the investigation/optimization of the Pd-catalyzed oxidative C–H/C–H coupling polymerization. The detailed experimental results are shown in Table 2. The polymerization for **P3** was first investigated under an atmosphere of N_2 in N,N-dimethyl-acetamide (DMAc) with Pd(OAc)$_2$, Cu(OAc)$_2$, and K$_2$CO$_3$. The results indicate that the palladium catalyst is necessary for the polymerization, and a 10% molar ratio of the Pd catalyst is the optimum amount (Table 2, entry 3). In addition, the same polymerization reaction could also be conducted in the presence of Ag$_2$CO$_3$ instead of Cu(II) as the co-catalyst (Table 2, entry 8). Although a narrow distribution of **P3** could be obtained using highly polar aprotic solvents DMSO and NMP, the yield and M_n decreased accordingly (Table 2, entries 5 and 6). A traditional polymerization oxidant FeCl$_3$ was not compatible under the reaction conditions (Table 2, entry 11), which may be attributed to the deficient electron

Table 2 Reaction conditions for the polymerization of **P3** by Pd-catalyzed oxidative C–H/C–H coupling[a]

Entry	Pd catalyst[b] (mol%)	Oxidant	Solvent	Additive	Yield[c] (%)	M_n (kDa)	PDI
1	5	Cu(OAc)$_2$	DMAc	K$_2$CO$_3$	74	16	1.34
2[d]	10	Cu(OAc)$_2$	DMAc	K$_2$CO$_3$	86	16	1.40
3	10	Cu(OAc)$_2$	DMAc	K$_2$CO$_3$	88	18	1.28
4	20	Cu(OAc)$_2$	DMAc	K$_2$CO$_3$	86	17	1.64
5	10	Cu(OAc)$_2$	NMP	K$_2$CO$_3$	77	9	1.05
6	10	Cu(OAc)$_2$	DMSO	K$_2$CO$_3$	59	8	1.04
7	10	Cu(OAc)$_2$	DMAc	—	76	19	1.46
8	10	Ag$_2$CO$_3$[e]	DMAc	—	54	15	1.59
9	10	—	DMAc	—	—	—	—
10	0	Cu(OAc)$_2$	DMAc	K$_2$CO$_3$	—	—	—
11	0	FeCl$_3$[f]	DMAc	—	—	—	—
12	0	Cu(OAc)$_2$	DMAc	KF/AgNO$_3$[g]	—	—	—
13	10	Cu(OAc)$_2$	DMAc	K$_2$CO$_3$	39	9	1.05
14	10	Cu(OAc)$_2$	DMAc	K$_2$CO$_3$	73	12	1.22

[a] Reaction conditions: substrate (1 equiv.), oxidant (2.1 equiv.), additive (2.2 equiv.) in 2 mL of DMAc at 110 °C in N_2 for 72 h. [b] Entries 1–9, Pd(OAc)$_2$ as the catalyst; entry 13, Pd(dppf)Cl$_2$ as the catalyst; entry 14, Pd(PhCN)$_2$Cl$_2$ as the catalyst. [c] Isolated yield after purification. [d] Reaction time was 48 h. [e] Ag$_2$CO$_3$ (4 equiv.). [f] FeCl$_3$ (6 equiv.). [g] KF/AgNO$_3$ = 1 : 2.1.
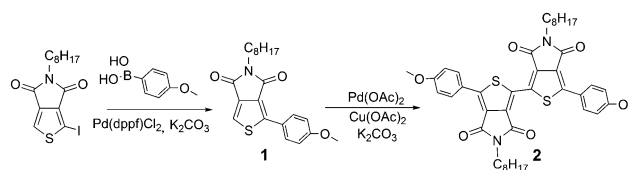
Scheme 2 The model reaction for the Pd-catalyzed oxidative C–H/C–H coupling.

at the 2-position of the substrate.[9] Other palladium catalysts such as Pd(dppf)Cl$_2$, Pd(PhCN)$_2$Cl$_2$ could also be used for the same synthesis (Table 2, entries 13 and 14).

In order to further confirm the Pd-catalyzed oxidative C–H/C–H coupling reaction, a model reaction was carried out as shown in Scheme 2, where a model small molecule **1** was designed and used for the coupling reaction. As expected, the product of bis(1-(4-methoxyphenyl)-5-octyl-5H-thieno[3,4-c]pyrrole-4,6-dione) was isolated with a high yield of 98% and confirmed using NMR and MS (see the ESI† for details).

Based on the above results, a polymerization mechanism is proposed as illustrated in Fig. 1. First, the intermediate **A** is formed as a six member ring by efficient coordination between the Pd(OAc)$_2$ catalyst and the substrate.[5] HOAc produced in the following step could be captured by potassium carbonate. A five membered cyclic intermediate B is then formed by the coordination of the carbonyl of the substrate (**M1**).[1e,2a,10] After reaction with another substrate, the species **C** was obtained. Cu(OAc)$_2$ serves as an oxidizing agent for the Pd(0) species to regenerate the Pd(II) catalyst.

The UV/Vis absorptions of the three polymers **P1**–**P3** in solution and in the solid state are presented in Fig. S21 (ESI†) and detailed information is presented in Table 3. **P1**–**P3** exhibited a broad absorption in the range 400–700 nm with maximum absorption at 461, 557 and 543 nm respectively in a chloroform solution. The solid film absorption spectra of these three
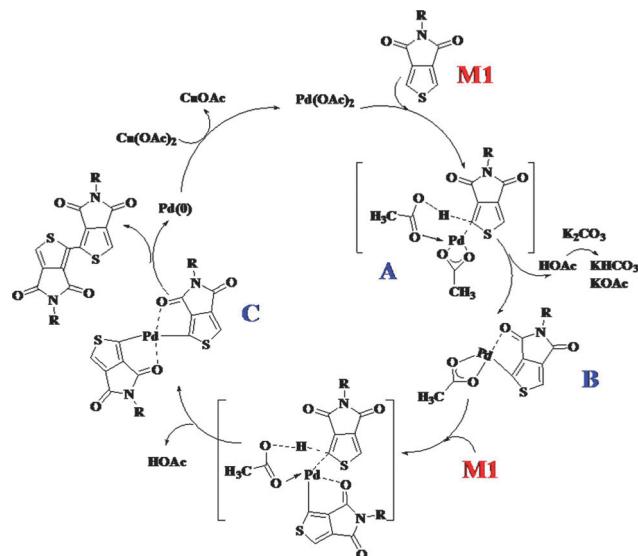
Fig. 1 Proposed reaction mechanism of the Pd-catalyzed oxidative C–H/C–H coupling reaction.

Table 3 Optical and electrochemical properties of **P1–P3**

Entry	$\lambda_{max}{}^{a}$ (nm)	$\lambda_{max}{}^{b}$ (nm)	$E_g^{\text{opt}\,c}$ (eV)	HOMO^{d} (eV)	LUMO^{d} (eV)
P1	461	538	1.92	−5.90	−3.98
P2	457	433	1.82	−5.78	−3.96
	557	575			
P3	458	433	1.85	−5.80	−3.95
	543	525			

^{a} From the UV-Vis absorption spectra in solution and film, respectively. ^{b} From the UV-Vis absorption spectra in solution and film, respectively. ^{c} Estimated from the onset absorption of the thin film. ^{d} E_g^{opt} = HOMO − LUMO (eV) and LUMO = − $e(E_{\text{onset}}^{\text{red}}$ + 4.8) (eV).

polymers all showed an obvious red shift (30–50 nm) compared to their corresponding solution absorption spectra. By extrapolation of the absorption onsets in the film state, the optical band gaps were estimated to be 1.92, 1.82 and 1.85 eV for **P1, P2** and **P3**, respectively, which are consistent with the values of 1.90, 1.76 and 1.81 eV, measured by cyclic voltammetry (CV) in the literature[11] (see also Table 3). Also, thermogravimetric analysis (TGA) suggested that these polymers exhibit excellent stability, with decomposition temperatures above 300 °C under a N_2 atmosphere (Fig. S22, ESI†). These data suggest that these polymers synthesized using our very mild and direct polymerization process could be used for optoelectronic applications.

In conclusion, a new catalytic oxidative polymerization method was developed using a Pd-catalyzed oxidative C–H/C–H

coupling with high yields in a more environmentally friendly manner, which avoids many issues using the conventional organometallic intermediates. Furthermore, a model reaction was carried out to verify the polymerization mechanism. We believe that upon conducting further research many versatile polymers for various optoelectronic applications could be obtained using this simple and direct polymerization method.

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