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COMMUNICATION

Synthesis of 5-alkyl[3,4-c]thienopyrrole-4,6-dione-based polymers by a Pd-catalyzed oxidative C-H/C-H homopolymerization reaction

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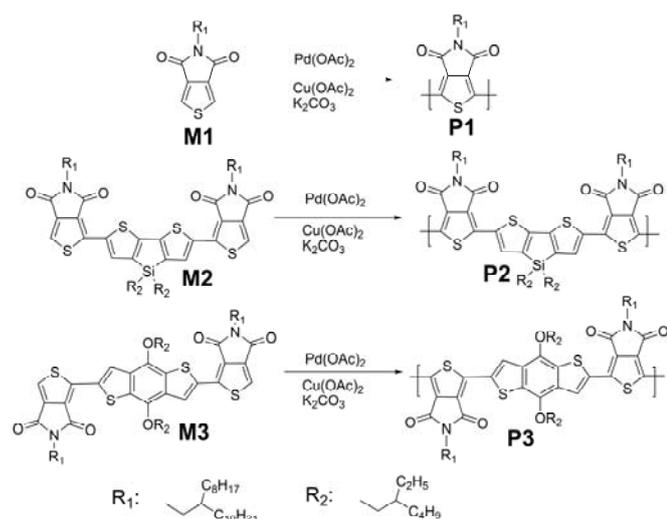
A new, simple, mild, atom economical homopolymerization method through Pd-catalyzed oxidative C-H/C-H coupling was developed for the preparation of a series of 5-alkyl[3,4-c]thienopyrrole-4,6-dione-based conjugated polymers.

Direct C-H/C-H coupling is obviously the best and most economical way to build new C-C bonds for new material synthesis, with many advantages such as more atom-economic, more diverse starting materials and avoiding the issue of end-capping groups.¹ Indeed, there have been some reports using this approach to make small molecules,^{1a,1b,1e} for example, bithiophene 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 done in most cases because the terminal halide or metal-containing functionalities are detrimental for the intrinsic properties of the corresponding polymer-based devices.^{3c,5}

Big advances come from the recent work, 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 is then 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 inter-mediate. This is especially greatly required for many functional photoelectronic polymers. Indeed, in our pursuit for organic/polymeric photovoltaic materials,⁸ a challenge often facing us is to achieve 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), dithienosilole (DTS) and benzo[1,2-b:4,5-b']dithiophene (BDT) based units, widely used as efficient building block 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 by Pd-catalyzed oxidative C-H/C-H coupling reactions with Pd(OAc)₂ as the catalyst in the presence of Cu(OAc)₂ and K₂CO₃ 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 chromatography (SEC) and thermogravimetric analysis (TGA) (see the ESI for details).



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

As shown in Table 1, **P1-P3** could be produced with high yields with a molecular weight 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 starting materials to perform the same polymerization under the same conditions after adding new catalyst to achieve even higher polymerization degrees (**P3''** with $M_n \sim 23$ kDa) (see polymerization procedure of **P3''** in the ESI for details), which allows a controlled molecular weight to be achieved.

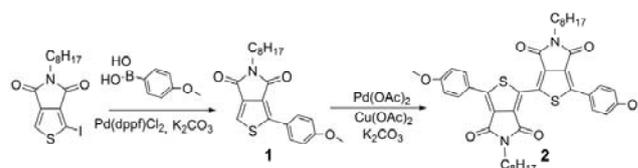
Table 1 Characterization of polymers **P1-P3**.^[a]

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.

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*-dimethylacetamide (DMAc) with $Pd(OAc)_2$, $Cu(OAc)_2$, and K_2CO_3 . The results indicate that the palladium catalyst is necessary for the polymerization, and 10% molar ratio of 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_2CO_3 instead of $Cu(II)$ as the co-catalyst (Table 2, entry 8). While a narrow distribution of **P3** could be obtained using high polar aprotic solvents DMSO and NMP, however, the yield and M_n decreased accordingly (Table 2, entries 5–6). A traditional polymerization oxidant $FeCl_3$ was not compatible for the reaction condition (Table 2, entry 11), which should be attributed to the deficient electron at 2-position of substrate.⁹ Other palladium catalysts such as $Pd(dppf)Cl_2$,

$Pd(PhCN)_2Cl_2$ could also be used for the same synthesis (Table 2, entries 13–14).



Scheme 2 The model reaction for the Pd-catalyzed oxidative C-H/C-H coupling.

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 by NMR and MS (see the ESI for details).

Based on 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 $Pd(OAc)_2$ 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**).^{1c,2a,10} After reacting with another substrate, specie **C** was obtained. $Cu(OAc)_2$ serves as an oxidizing agent of $Pd(0)$ species to regenerate the $Pd(II)$ catalyst.

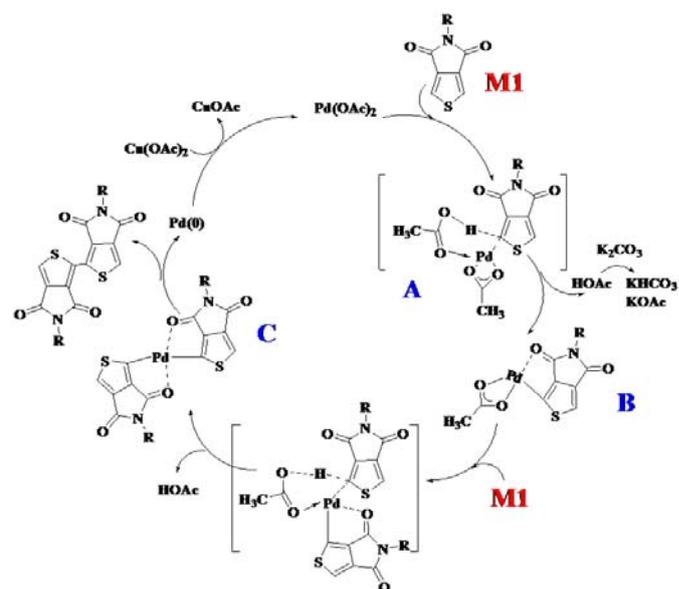


Fig. 1 Proposed reaction mechanism of the Pd-catalyzed oxidative C-H/C-H coupling reaction.

The UV/Vis absorptions of the three polymers **P1-P3** in solution and the solid state are presented in Fig. S21 and detailed information is presented in Table 3. **P1-P3** exhibited 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 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 literatures¹¹

(Also see Table 3). Also, thermogravimetric analysis (TGA) suggested that these polymers exhibited excellent stability, with decomposition temperatures above 300 °C under a N₂ atmosphere (Fig. S22). These data suggest that these polymers synthesized using our very mild and direct polymerization process could be used for optoelectronic applications.

Table 2 Reaction conditions for the polymerization of **P3** by Pd-Catalyzed Oxidative C-H/C-H coupling.^[a]

Entry	Pd catalyst (mol%) ^[b]	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 N₂ for 72 h. [b] entries 1-9, Pd(OAc)₂ as catalyst; entry 13, Pd(dppf)Cl₂ as catalyst; entry 14, Pd(PhCN)₂Cl₂ as catalyst. [c] Isolated yield after purification. [d] Reaction time was 48h. [e] Ag₂CO₃ (4 equiv). [f] FeCl₃ (6 equiv). [g] KF/AgNO₃=1:2.1.

Table 3 Optical and electrochemical properties of **P1-P3**.

Entry	λ _{max} ^[a] (nm)	λ _{max} ^[b] (nm)	E _g ^{opt} ^[c] (eV)	HOMO ^[d] (eV)	LUMO ^[d] (eV)
P1	461	538	1.92	-5.90	-3.98
P2	457 557	433 575	1.82	-5.78	-3.96
P3	458 543	433 525	1.85	-5.80	-3.95

[a] and [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_{onset}^{red} + 4.8) (eV).

In conclusion, a new catalytic oxidative polymerization method was developed using 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 to verify the polymerization mechanism. We believe that many versatile polymers for various optoelectronic applications could be obtained using this simple and direct polymerization method after further research.

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