

An Efficient Catalytic System for Room-temperature Stille Polymerization

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Electronic Supplementary Information

Abstract Donor-acceptor conjugated polymers are vital materials for organic electronics, but traditional thermally driven Stille polymerization suffers from unavoidable homocoupling defects and batch variations. In this study, we developed an efficient room-temperature Stille catalytic system using $P(t-Bu)_3Pd(crotyl)Cl$ as the precatalyst and CsF as the base. This method displays broad substrate universality, affording various conjugated polymers with fewer homocoupling fragments than the traditional methods. This work provides a mild, general route toward high-performance, regio-regular conjugated polymers.

Keywords Room-temperature Stille polymerization; Conjugated polymers; Homocoupling; Organic solar cells

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INTRODUCTION

Donor-acceptor (D-A) type conjugated polymers (CPs) are core materials for modern organic electronics and organic solar cells (OSCs), endowed with tunable chemical structures, adjustable energy gaps, excellent mechanical flexibility, and solution processability, enabling large-area printing fabrication.^[1–3] The precise construction of D-A alternating conjugated skeletons *via* cross-coupling polymerization is the key to realizing the excellent optoelectronic properties of such polymers, and palladium-catalyzed Stille cross-coupling polymerization has long been recognized as one of the most efficient synthetic strategies for D-A CPs. This method features high functional group tolerance and high reaction yields, making it the mainstream choice for preparing well-defined conjugated polymers.^[4–6] However, traditional thermally activated Stille polymerization is commonly catalyzed by $Pd(II)$ catalysts or air-unstable $Pd(0)$ catalysts.^[4,7] Both $Pd(II)$ and oxidized $Pd(0)$ species are prone to induce homocoupling of organotin nucleophiles.^[8] In addition, the $Ar-Pd(II)-X$ species formed *via* oxidative addition of the $Pd(0)$ catalyst can undergo a reduction reaction to generate $Ar-Pd(0)^-$ species, which are susceptible to a second oxidative addition, thereby resulting in the homocoupling of aryl dibromide elec-

trophiles.^[8] Homocoupling defects can affect the molecular packing and spectral properties of conjugated polymers.^[9–12] Moreover, the homocoupling content is difficult to predict and control, which inevitably leads to significant batch-to-batch variation during polymer synthesis.^[13] Traditional thermally activated Stille polycondensation cannot produce polymers with low homocoupling defects, which has become a critical bottleneck restricting the development and large-scale preparation of CPs.^[14]

The development of room-temperature (RT) Stille polymerization is a promising strategy to minimize homocoupling defects. In addition, RT polymerization offers the advantages of low energy consumption, simple operation, and reduced chemical consumption. However, the development of RT Stille polymerization has long been stagnant compared with the relatively mature RT Suzuki–Miyaura cross-coupling polymerizations,^[12,15–17] mainly because of the lack of highly reactive palladium catalytic systems that can reduce the transition state energy barrier of the Stille cross-coupling reaction and drive polymerization efficiently under mild conditions.^[18] According to the reaction mechanism of Pd -catalyzed Stille cross-coupling, conventional Stille reactions employing either $Pd(II)$ or $Pd(0)$ precursors require the assistance of ligands and heating to generate catalytically active 14-electron $Pd(0)L_2$ species, as well as highly reactive 12-electron $Pd(0)L$ complexes.^[19–25] As $Pd(0)L$ species are highly unstable and cannot be directly prepared or isolated,^[25] the *in situ* generation of such active species *via* RT activation of precatalyst is crucial for the progress of RT Stille reactions. In addition, ow-

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ing to the extremely large steric cone angle of the $P(t\text{-Bu})_3$ ligand, the coordinated $Pd(0)$ complexes spontaneously dissociated one phosphine ligand to generate highly reactive monoligated $L_1Pd(0)$ species, which significantly reduced the activation barrier for oxidative addition and enabled efficient RT Stille polymerization. In contrast, small steric phosphine ligands (e.g., PPh_3) tend to retain stable bis-ligated $L_2Pd(0)$ structures with low reactivity, thus requiring high-temperature polymerization conditions. This is further supported by previous DFT studies showing the far higher aryl halide reactivity of $L_1Pd(0)$ over $L_2Pd(0)$ in the $P(t\text{-Bu})_3$ catalytic system.^[19,25,26]

Based on Buchwald's palladacycle precatalysts, which can be activated by weak base to produce $Pd(0)L$ at RT,^[27–29] recent research has developed an RT Stille polymerization method using $P(t\text{-Bu})_3Pd$ G3 as the precatalyst and K_3PO_4 as the base, and successfully synthesized 12 kinds of high-molecular-weight D-A type CPs with minimal homocoupling defects.^[30] However, limited by the types of electron-deficient and electron-donating units, D-A polymers constructed based on this catalyst system are relatively monolithic in structure. Furthermore, carbazole, a byproduct generated upon activation of the precatalyst,^[28] carries the risk of end-capping the polymer *via* Pd-catalyzed C–N cross-coupling.^[8] Moreover, for the synthesis of state-of-the-art polymer donors and acceptors in OSCs, the compatibility between the RT Stille polymerization system and the structural characteristics of photovoltaic monomers, together with the influence of the polymerization process on the photovoltaic properties of the final polymers, still requires in-depth investigation.

In this work, we focused on the synthesis of classic photovoltaic conjugated polymers and carried out systematic optimization and innovation of the RT Stille polymerization system. Taking the representative benzodithiophene (BDT)-based polymer donor J60 as the template, we systematically investigated the effects of base type and dosage, palladium catalyst loading, reaction solvent, and reaction time on the polymerization yield, number-average molecular weight (M_n), and polydispersity ($\bar{D}$) of the target polymer, and screened out a high-efficiency RT catalytic system with $P(t\text{-Bu})_3Pd(crotyl)Cl$ as the precatalyst,^[25] and CsF as the base. On this basis, we verified the broad substrate universality of this optimized system by synthesizing a series of D-A type conjugated polymers (including classic photovoltaic materials such as PBDB-T, PM6, and N2200) even random terpolymers with different structural characteristics. Through small molecule model reactions and 1H nuclear magnetic resonance (1H -NMR) spectroscopy, we confirmed that this catalytic system can effectively reduce the homocoupling of both aryl dibromide electrophilic and organotin nucleophilic monomers, and that the resulting polymers have significantly reduced structural defects compared to those prepared by traditional thermal Stille polymerization and the reported RT $P(t\text{-Bu})_3Pd$ G3/ K_3PO_4 system. Furthermore, we fabricated organic photovoltaic devices with several polymers synthesized by this method as the active layer, and the device performance test results showed that the polymers prepared by the optimized RT Stille polymerization exhibited higher power conversion efficiency (PCE) than the polymer samples synthesized *via* the thermally activated $Pd(PPh_3)_4$ system.

EXPERIMENTAL

The detailed polymerization optimization and synthetic procedures of all polymers are shown in the electronic supplementary information (ESI).

RESULTS AND DISCUSSION

Polymerization Optimization

To optimize the polymerization reaction conditions, a representative polymer donor, named J60 from the J-series polymers was selected as the template polymer, as shown in Fig. 1(a). Nucleophile N1 ((4,8-bis(5-((2-ethylhexyl)thio)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(trimethylstannane)) and electrophile E1 (4,7-bis(5-bromothiophen-2-yl)-5,6-difluoro-2-(2-hexyldecyl)-2H-benzo[d][1,2,3]triazole) were used to perform polymerization.

The RT polymerization was systematically optimized under various conditions, as shown in Table 1 and Fig. 1(b) illustrates a plausible activation mechanism of the $P(t\text{-Bu})_3Pd(crotyl)Cl$ precatalyst. The precatalyst initially exists as an η^3 -crotyl $Pd(II)$ complex, which can isomerize to the corresponding η^1 - σ -allyl species. In the presence of an alkali metal salt base (A^+M^+), the η^1 -crotyl ligand undergoes nucleophilic substitution, releasing a functionalized butene derivative (product A) and forming the salt byproduct M^+Cl^- . Concurrently, the $Pd(II)$ center is reduced to the catalytically active monoligated $Pd(0)$ species, which enters the catalytic cycle.^[27] This process underscores the role of the crotyl ligand as a sacrificial group to generate the active $Pd(0)$ catalyst and highlights that precatalyst activation is closely related to the nucleophilicity of the base used. Therefore, we carried out systematic investigation and careful screening of the bases. Experiments demonstrated that the use of TMSOK, *t*-BuOK, Cs_2CO_3 , K_3PO_4 and KF (entries 1–5) with 5 mol% $P(t\text{-Bu})_3Pd(crotyl)Cl$ precatalyst and THF as the solvent failed to effectively drive the polymerization at RT. Specifically, no product was formed with TMSOK, whereas only oligomers were obtained with Cs_2CO_3 and K_3PO_4 , which were not isolated due to the minimal products. When potassium fluoride (KF) was used as the base in the reaction system (entry 5), the resulting oligomers were still soluble in *n*-hexane. This synthetic route afforded a higher quantity of crude product, with an overall yield of 35.8% after isolation *via* Soxhlet extraction, indicating that a stronger nucleophilic base could be beneficial for the activation of the precatalyst. Therefore, replacing KF with the stronger base CsF can make the polymerization reaction proceed more efficiently. Fig. 1(c) shows the rapid evolution of reaction mixture color over time. After reacting at RT for 2 h, the polymer achieved a promising M_n of 14.46 kDa, with a yield of 57.7% (entry 6), which demonstrates that the appropriate selection of a base plays a crucial role in the activation of the catalyst (Fig. 1b). In addition, the results of entry 7 reveal that when the reaction time remained unchanged, raising the precatalyst loading from 5 mol% to 10 mol% afforded the target polymer with an M_n of 19.59 kDa. This observation demonstrates that a precatalyst loading of 10 mol% is more favorable for efficient polymerization. Further extending the reaction time to 24 h enabled the target polymer to reach a higher M_n value of 39.47 kDa with a simi-

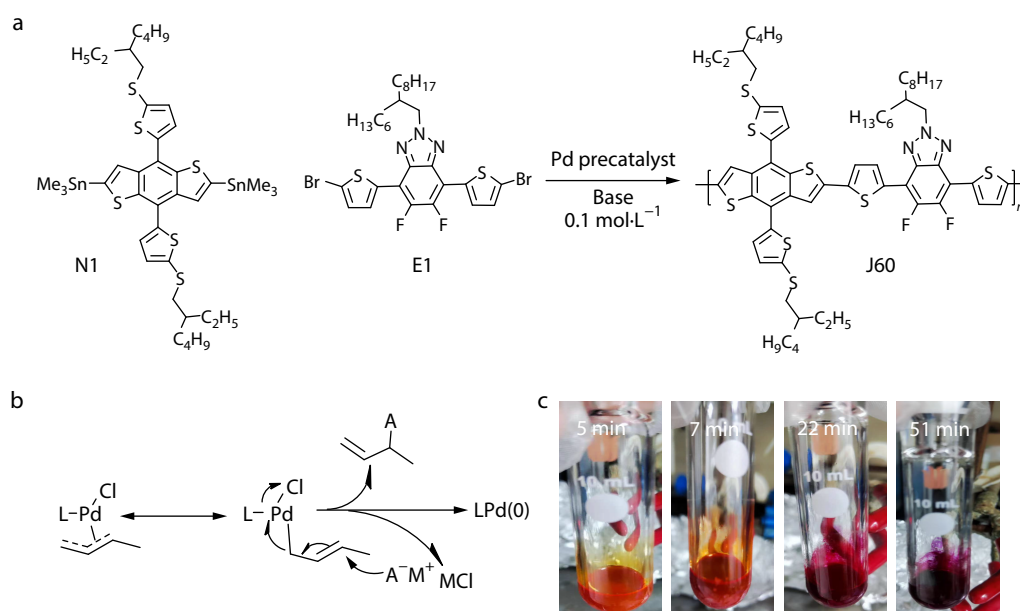


Fig. 1 (a) Synthetic procedure of J60; (b) The plausible activation pathway of LPd(crotyl)Cl precatalyst; (c) Images of the reaction mixture color evolution over time.

Table 1 Optimization of polymerization conditions.

Entry	Catalyst	Catalyst loading (mol%)	Base	Solvent	M_n (kDa)	$\bar{D}$	Time (h)	Yield (%)
1	P(<i>t</i> -Bu) ₃ Pd(crotyl)Cl	5	TMSOK (2.5 equiv.)	THF	/	/	2	/
2	P(<i>t</i> -Bu) ₃ Pd(crotyl)Cl	5	<i>t</i> -BuOK (2.5 equiv.)	THF	/	/	2	/
3	P(<i>t</i> -Bu) ₃ Pd(crotyl)Cl	5	K ₃ PO ₄ (2.5 equiv.)	THF	/	/	2	/
4	P(<i>t</i> -Bu) ₃ Pd(crotyl)Cl	5	Cs ₂ CO ₃ (2.5 equiv.)	THF	/	/	2	/
5	P(<i>t</i> -Bu) ₃ Pd(crotyl)Cl	5	KF (2.5 equiv.)	THF	/	/	2	35.8
6	P(<i>t</i> -Bu) ₃ Pd(crotyl)Cl	5	CsF (2.5 equiv.)	THF	14.46	1.83	2	57.7
7	P(<i>t</i> -Bu) ₃ Pd(crotyl)Cl	10	CsF (2.5 equiv.)	THF	19.59	2.54	2	58.6
8 ^a	P(<i>t</i> -Bu) ₃ Pd(crotyl)Cl	10	CsF (2.5 equiv.)	THF	39.47	1.84	24	69.9
9	P(<i>t</i> -Bu) ₃ Pd(crotyl)Cl	10	CsF (2.2 equiv.)	THF	20.85	1.78	24	65.1
10	P(<i>t</i> -Bu) ₃ Pd(crotyl)Cl	10	CsF (3 equiv.)	THF	25.80	2.22	13	80.5
11	P(<i>t</i> -Bu) ₃ Pd(crotyl)Cl	10	CsF (3 equiv.)	THF	31.82	1.85	24	70.9
12	P(<i>t</i> -Bu) ₃ Pd(crotyl)Cl	10	KF (3 equiv.)	THF	31.49	2.29	24	71.3
13	P(<i>t</i> -Bu) ₃ Pd(crotyl)Cl	10	CsF (2.5 equiv.)	Toluene	4.53	1.40	2	40.1
14	P(<i>t</i> -Bu) ₃ Pd(crotyl)Cl	10	CsF (2.5 equiv.)	CB	3.89	1.40	2	36.3
15	P(<i>t</i> -Bu) ₃ Pd G3	10	K ₃ PO ₄ (1.0 equiv.)	THF	18.46	1.84	24	65.6

^a Entry 8 demonstrates the optimal condition: 10 mol% P(*t*-Bu)₃Pd(crotyl)Cl, 2.5 equiv. CsF and reaction time of 24 h.

lar $\bar{D}$ of 1.84 and higher yield of 69.9% (entry 8). To further optimize the polymerization reaction conditions, we investigated the effect of varying the equiv. of CsF. When the dosage of CsF was 2.2 and 3.0 equiv. (entries 9 and 11), the M_n s of the resulting polymers were 20.85 and 31.32 kDa, with the corresponding $\bar{D}$ values of 1.78 and 1.85, respectively. To finally identify the optimal base, we adjusted the loading of KF to 3

equiv. (entry 12) while keeping all other reaction parameters identical to those of entry 11. The resulting polymer possessed an M_n of 31.49 kDa with a $\bar{D}$ of 2.29, and an isolated yield of 71.3%. Evidently, KF delivered slightly inferior performance relative to CsF. These results indicate that the optimal amount of CsF is 2.5 equiv., and the $\bar{D}$ exhibits a gradual increase with the rising equiv. of this base. In addition, to fur-

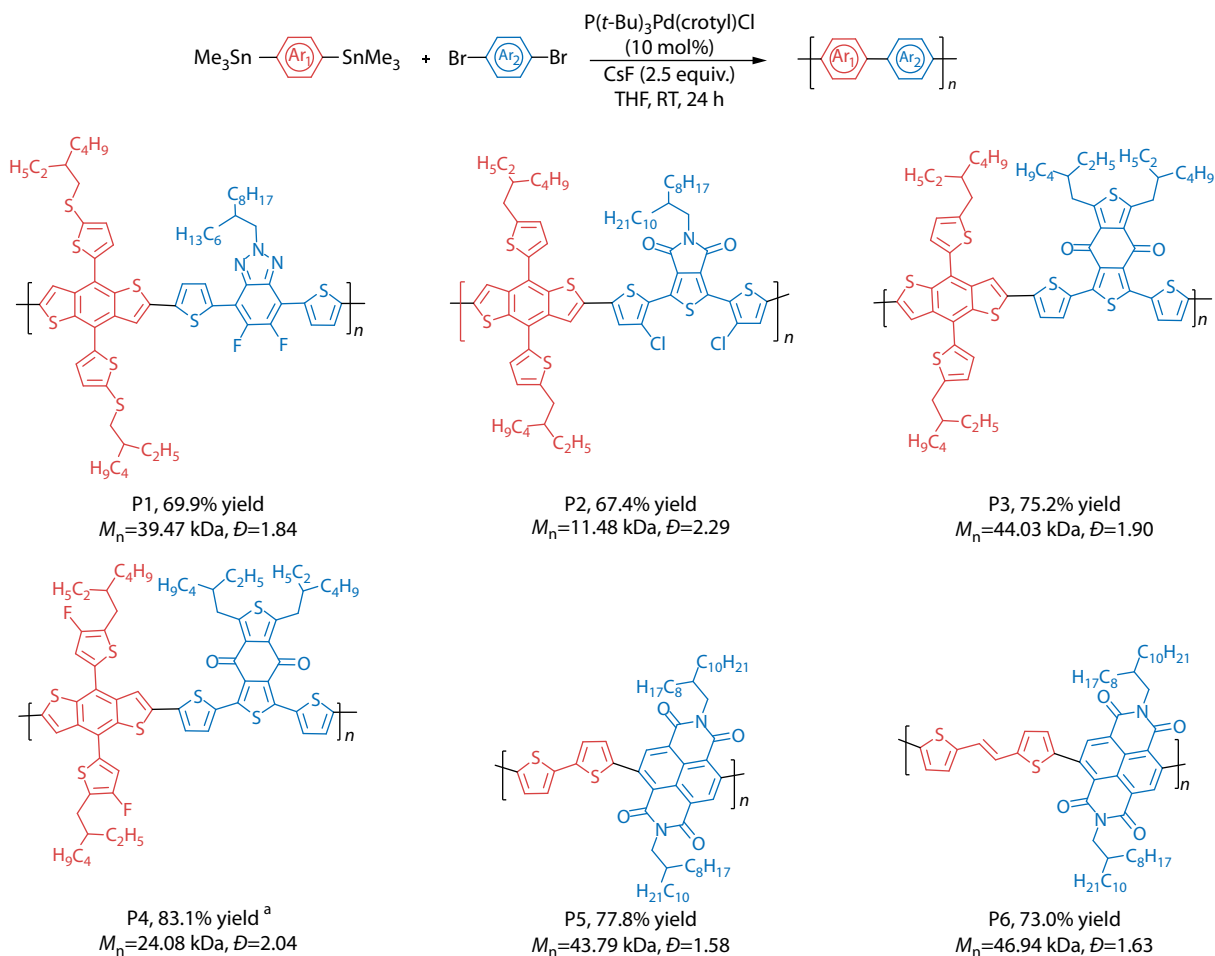
ther screen the reaction solvents, the commonly employed solvents in Stille polycondensation, toluene and chlorobenzene, were also attempted to synthesize the polymer. The experimental results showed that when toluene and chlorobenzene were used as the reaction solvents, the obtained polymers exhibited extremely low M_n s of only 4.53 and 3.89 kDa, respectively (entries 13 and 14). These results indicate that THF, a solvent with higher polarity, is more conducive to the proceeding of the RT Stille polycondensation compared with toluene and chlorobenzene with lower polarities. In contrast, employing the reported RT Stille polymerization conditions (entry 15) yielded polymer J60 with a lower molecular weight (M_n =18.46 kDa) and reduced yield of 65.6%, thereby underscoring the superior effectiveness of the optimal conditions established in this work.

Substrate Scope

Inspired by the above success, we next examined the generality of the present RT Stille polymerization methodology. A series of electrophiles (E1–E9) and nucleophiles (N1–N7) were investigated and afforded. The summarized polymerization results under the optimal reaction conditions are shown in Fig. 2. The UV-Vis absorption spectra in dilute chloroform solution, ^1H -NMR spectra and GPC curves of the corresponding polymers are shown in Fig. S2, Figs. S33–S53 and Figs. S54–S77 (in ESI), respectively.

For polymer substrates constructed based on the benzodithiophene (BDT) unit, the alkylthiophene side-chain-substituted BDT monomer N2 ((4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(trimethylstannane)) exhibited excellent copolymerization reactivity with a variety of electrophilic monomers. For instance, polycondensation of N2 with E3 (1,3-bis(5-bromothiophen-2-yl)-5,7-bis(2-ethylhexyl)-4*H*,8*H*-benzo[1,2-*c*:4,5-*c'*]dithiophene-4,8-dione) afforded polymer P3 (PBDB-T) in 75.2% yield, with a high M_n value of 44.03 kDa and a $\bar{D}$ of 1.90. When N2 was copolymerized with the representative thienopyrrolodione (TPD)-based unit E6 (1,3-dibromo-5-(2-hexyldecyl)-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione), polymer P11 (M_n =23.44 kDa, $\bar{D}$ =2.10) was obtained in 64.0% yield. However, copolymerization of N2 with the chlorine-containing TPD-based monomer E2 (1,3-bis(5-bromo-3-chlorothiophen-2-yl)-5-(2-octyldodecyl)-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione) led to a dramatic decrease in the M_n of the target polymer P2, which dropped to only 11.48 kDa.

Subsequently, we investigated the effect of fluorine substitution on the polymerization activity of the BDT monomer. The fluorinated monomer N3 ((4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(trimethylstannane)) was copolymerized with E3 to yield polymer P4, also known as PBDB-TF or PM6. Compared to the non-fluorinated polymer P3, the M_n of P4 decreased signifi-



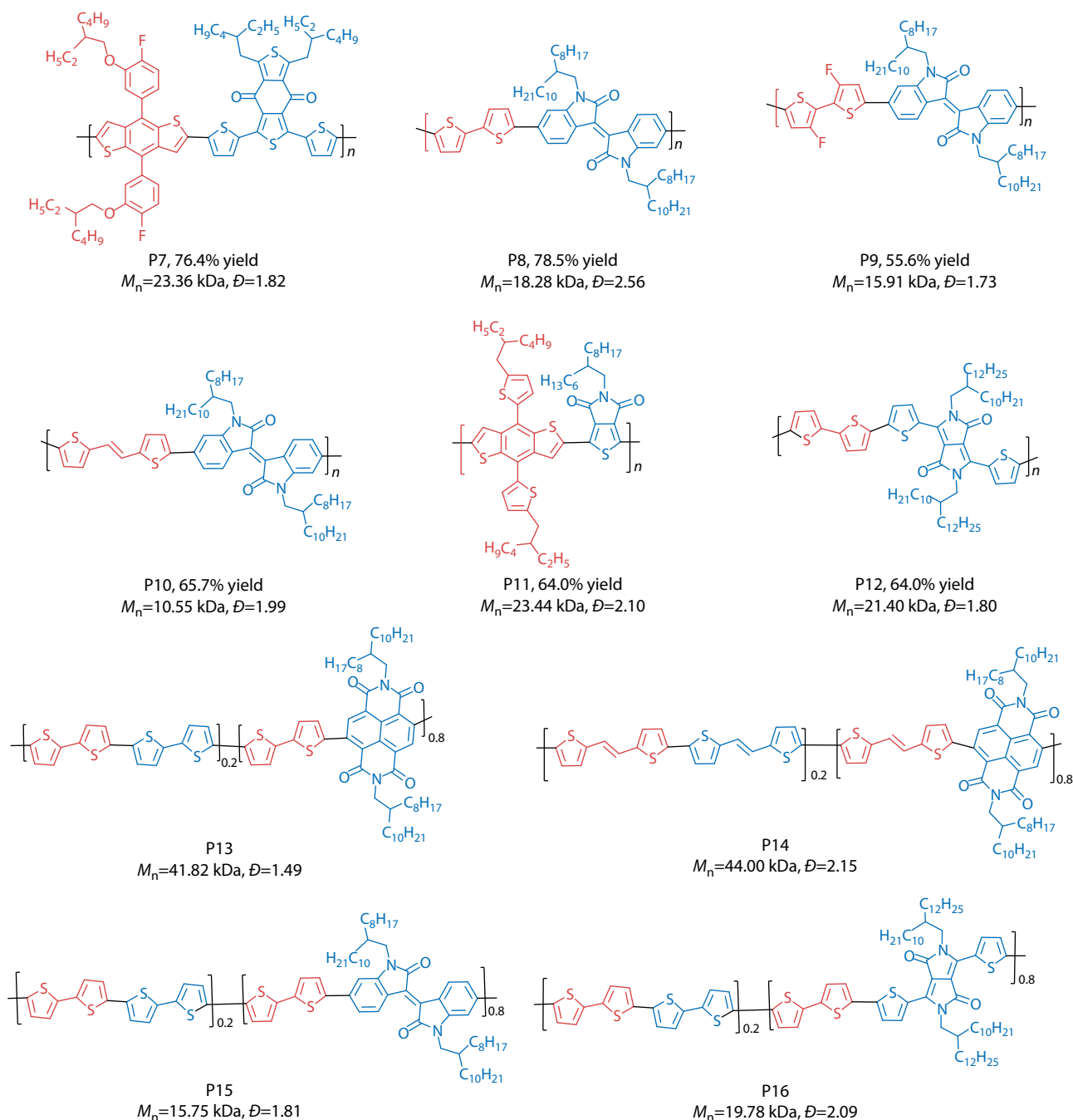


Fig. 2 Substrate scope of the modified RT Stille polymerization synthesized using the optimized conditions except $0.2 \text{ mol}\cdot\text{L}^{-1}$, 40°C .

cantly to 24.08 kDa. To investigate the batch-to-batch reproducibility of the polymerization, five additional batches and scalable synthesis of P4 were performed under the optimized conditions (Table S1 in ESI). The five batches of P4 exhibited similar molecular weights (M_n : 19.7–22.4 kDa, $\bar{D}$: 1.72–1.97) with consistently high yields of over 80% and their absorption spectra showed negligible differences (Fig. S2 in ESI), demonstrating the excellent reproducibility of this synthetic method. Furthermore, P4 was successfully synthesized on a scale of over 0.5 g (Table S1 in ESI), with $M_n=18.3$ kDa, $\bar{D}=1.82$, and a yield of 82.7%, confirming that this polymerization is readily scalable for potential commercial applications.

Similarly, another fluorinated nucleophilic monomer N7 ((4,8-bis(3-((2-ethylhexyl)oxy)-4-fluorophenyl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(trimethylstannane)) was copolymerized with E3, producing polymer P7 with an M_n of 23.36 kDa, which is markedly lower than that of P3. This preliminary result suggests that fluorination of the nucleophilic monomer exerts an inhibitory effect on polymerization. This is mainly attributed to the electron-withdrawing effect of fluorine atoms, which reduces the electron-donating capacity of the α -carbon atom and thus decreases the reactivity of the transmetalation process, which is the rate-determining step of Stille coupling (see Fig. S79 in ESI for further interpreta-

tion).^[31–33] In addition to exploring wide energy gap (E_g) conjugated polymer substrates, we extended our investigation to narrow E_g conjugated polymers. Under the optimized reaction conditions, E4 (4,9-dibromo-2,7-bis(2-octyldodecyl)benzo[Imn][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone) was copolymerized with N5 (5,5'-bis(trimethylstannyl)-2,2'-bithiophene) and N6 ((*E*)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene) to synthesize the representative naphthalene diimide (NDI)-based polymer acceptor materials P5 (N2200) and P6 (PNDI-TV), in high yields of 77.8% and 73.0%, respectively. Both materials exhibited high M_n values of 43.79 and 46.94 kDa, respectively. Furthermore, several conjugated polymers based on dye molecules were synthesized, including a diketopyrrolopyrrole (DPP)-based polymer (P12) and isoindigo-based polymers (P8, P9, and P10). A comparison of the experimental data for P8 (M_n =18.28 kDa, $\bar{D}$ =2.56, yield=78.5%) and P9 (M_n =15.91 kDa, $\bar{D}$ =1.73, yield=55.6%) further confirms that fluorine substitution on the nucleophilic monomer hinders the transmetalation process, thereby limiting polymer chain growth. Finally, we explored the applicability of this RT Stille polymerization method for the synthesis of random terpolymers. Under the optimized conditions, four random terpolymers, designated as P13 (M_n =41.82 kDa, $\bar{D}$ =1.49), P14 (M_n =44.00 kDa, $\bar{D}$ =2.15), P15 (M_n =15.75 kDa, $\bar{D}$ =1.81), and P16 (M_n =19.78 kDa, $\bar{D}$ =2.09), were successfully synthesized, which underscores this methodology's broad applicability and potential for constructing complex, well-defined conjugated polymers under mild conditions.

Homocoupling Analysis

To explore the effectiveness of RT conditions in mitigating homocoupling defects during Stille polymerization, D-D'-D and D-A-D type small-molecule models were utilized, as shown in Fig. 3(a). We first conducted small-molecule model reactions between electrophile SE1 (bromobenzene) and nucleophile SN1 (2,5-bis(trimethylstannyl)thiophene). Impressively, no homocoupling products of either SE1 or SN1 were detected by gas chromatography-mass spectrometry under our RT Pd(crotyl)P(*t*-Bu₃)Cl/CsF catalytic system (Fig. S1 in ESI), confirming its intrinsic potential to suppress undesired homocoupling side reactions.

As shown in Fig. 3(b), the substrate scope of D-A-D-type conjugated small molecules was systematically investigated using a series of electron-deficient electrophiles and thiophene-based nucleophiles (tributyl(thiophen-2-yl)stannane and tributyl(4-octylthiophen-2-yl)stannane). The occurrence of side reactions was evaluated, and a direct comparison with the reported P(*t*-Bu)₃Pd G3/K₃PO₄ catalytic system was performed. For the synthesis of S1, the developed catalytic system afforded the target product in an excellent yield of 88.9%, outperforming the P(*t*-Bu)₃Pd G3/K₃PO₄ system which gave a notably lower yield of 69.2%. Meanwhile, the primary byproduct from homocoupling of E6 (1,3-dibromo-5-(2-hexyldecyl)-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione) was isolated in only 3.1% yield, far below the level observed with the conventional system. Similar trends were observed in the synthesis of S7, a structural analog of S1. The P(*t*-Bu)₃Pd(crotyl)Cl/CsF system delivered a higher yield and reduced homocoupling than the P(*t*-Bu)₃Pd G3/K₃PO₄ system.

For the cross-coupling of the strongly electron-deficient

electrophile SE5 (2,5-dibromothiophene-3-carbonitrile) with tributyl(4-octylthiophen-2-yl)stannane, both catalytic systems afforded the desired product S5 with comparable good efficiency, though homocoupling of SE5 was detected in both cases. In contrast, no homocoupling byproducts were observed for the bulky electron-deficient electrophile SE3 (1,3-dibromo-5,7-bis(2-ethylhexyl)-4*H*,8*H*-benzo[1,2-*c*:4,5-*c'*]dithiophene-4,8-dione) and the weakly electron-withdrawing electrophile SE4 (1,4-dibromo-2,5-difluorobenzene) under the P(*t*-Bu)₃Pd(crotyl)Cl/CsF conditions.

Collectively, these results demonstrate that P(*t*-Bu)₃Pd(crotyl)Cl/CsF system can fully suppress homocoupling of the model substrates bromobenzene and 2,5-bis(trimethylstannyl)thiophene, and generally delivers higher target product yields and lower homocoupling side product levels for D-A-D-type conjugated small molecule synthesis compared to the conventional Pd(PPh₃)₄ and P(*t*-Bu)₃Pd G3/K₃PO₄ systems. Furthermore, the results illustrate that the electronic properties and steric hindrance of the electrophilic substrates exert a pronounced effect on homocoupling.

Most conjugated polymers exhibit strong intermolecular aggregation, which induces severe peak broadening in their ¹H-NMR spectra and thus precludes high-precision structural elucidation. To address this limitation, polymers P5 and P6 were selected as model systems, which enabled unambiguous structural characterization *via* ¹H-NMR spectroscopy. These two polymers were further synthesized *via* conventional thermally driven and RT Stille polycondensation using the Pd(PPh₃)₄ (P5a and P6a) and P(*t*-Bu)₃Pd G3/K₃PO₄ (P5b and P6b) as catalytic systems, respectively. We then performed a comparative analysis of these spectra with those of the corresponding reference polymers P13, P14, which contain well-defined nucleophile homocoupling segments, to systematically investigate how different synthetic protocols modulate the occurrence of homocoupling side reactions. As shown in Fig. 3(c), in comparison with P13, no characteristic signals for bithiophene homocoupling were observed in the spectrum of P5, whereas such signals were detected in the 7.25–7.19 ppm range for P5a and P5b. As illustrated in Fig. 3(d), based on the methylene proton signals on the NDI imide, no significant peak was observed in the high-field region adjacent to the main peak, indicating the absence of NDI homocoupling defects in these samples. The homocoupling ratio α of the bithiophene in P5, P5a and P5b can be quantitatively estimated using the reported methods. The α values for P5, P5a and P5b are 8.2%, 14% and 12%, respectively (Fig. 3g).

Further analysis of another NDI-based polymer, P6, revealed distinct (*E*)-1,2-di(thiophen-2-yl)ethene (TVT) homocoupling signals in the range from 7.08 ppm to 7.98 ppm in the ¹H-NMR spectrum of P14, as shown in Fig. 3(e). A comparison of this spectrum with those of P6, P6a, and P6b showed that P6b contained a small amount of TVT homocoupling fragments, while no obvious signals were observed in this region for P6a. Additionally, as shown in Fig. 3(f), examination of the methylene proton signals on the NDI imide nitrogen atom revealed a small peak at 3.97 ppm in the high-field region adjacent to the main peak at 4.12 ppm in the spectrum of P6b, indicating the presence of a small amount of NDI homocoupling segments.^[34] In summary, a catalyst system

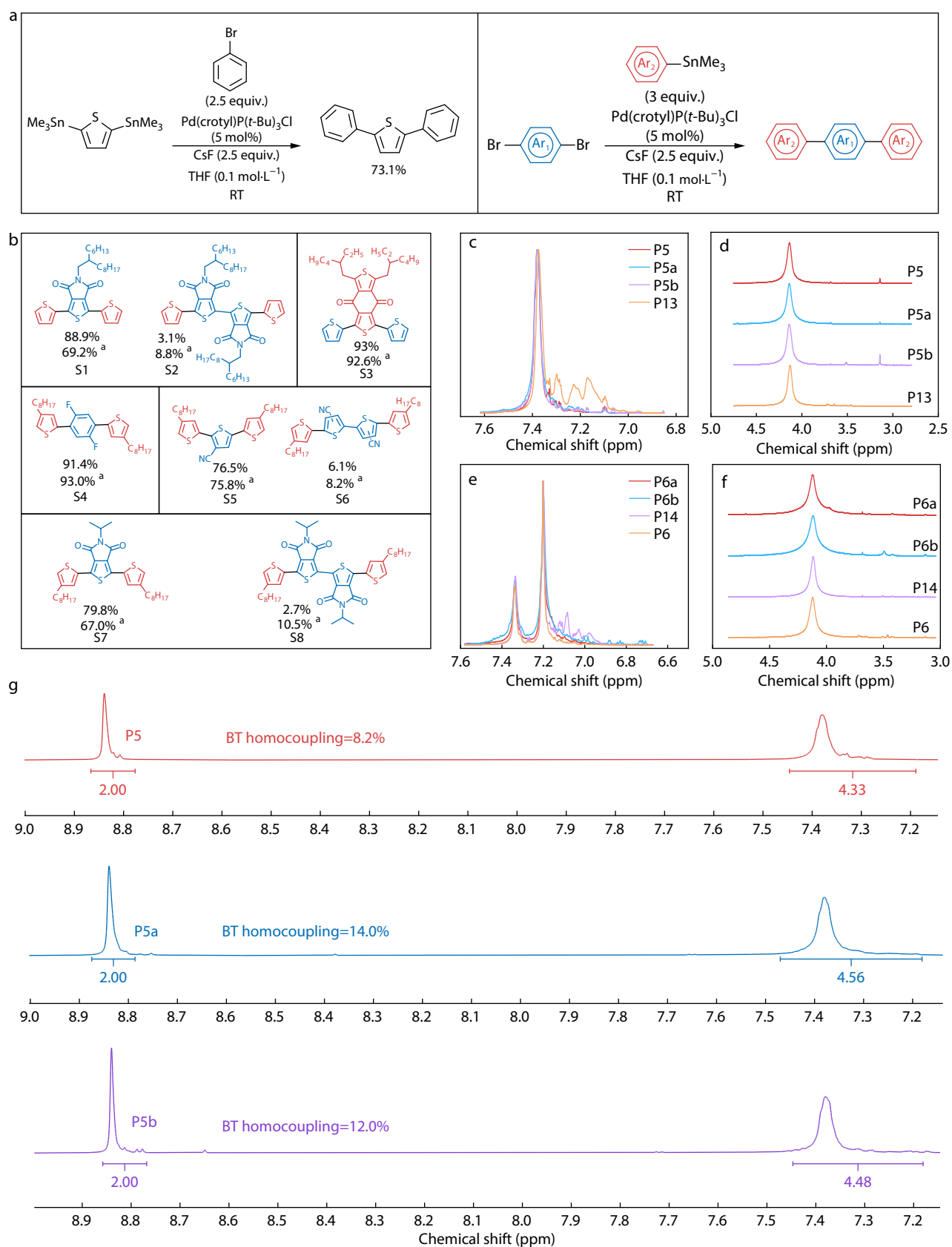


Fig. 3 (a, b) Side reaction analysis of small-molecule model reactions. ^a synthesized using the P(*t*-Bu)₃Pd G3/K₃PO₄ catalytic system; (c, d) ¹H-NMR spectra of P5, P5a, P5b and P13; (e, f) ¹H-NMR spectra of P6, P6a, P6b and P14 in CD₂Cl₄ at 333 K; (g) The aromatic region (9.00–7.14 ppm) of ¹H-NMR for P5, P5a, and P5b in C₂D₂Cl₄ at 333 K.

based on $P(t\text{-Bu})_3\text{Pd}(\text{crotyl})\text{Cl}/\text{CsF}$ effectively reduces the formation of homocoupling defects in both D and A units.

To verify whether the polymer materials synthesized *via* this catalytic system are suitable for organic photovoltaic devices, we fabricated organic solar cell devices based on polymer donors P1 (J60), P3 (PBDB-T) and P4 (PM6), along with polymer acceptors P5 (N2200) and P6 (PNDI-TVt).^[35] and systematically characterized their photovoltaic performance. The synthesized P1, P3, P4, P5 and P6 exhibit quite satisfactory PCEs. However, the synthesized PM6 exhibits unsatisfactory performance with a PCE of only 15.12%, which is far inferior to the 17.81% PCE for commercial PM6 materials. Such a large performance gap can be largely attributed to the high sensitivity of PM6 device performance to its molecular weight.^[36] The relative *J-V* curves and detailed photovoltaic parameters are shown in Figs. S3, S4 and Table S6 (in ESI).

To further elucidate the impact of homocoupling on photovoltaic device performance N2200 (P5 and P5a), a well-established polymeric acceptor, was selected as our research subject. As shown in Fig. S4(a) in ESI, the P5-based device achieves a higher PCE of 8.55%, compared with 6.3% for the P5a-based counterpart. The large disparity in device performance primarily stems from the higher open-circuit voltage (V_{OC}) of P5 (0.790 V) relative to P5a (0.742 V), alongside its distinctly superior fill factor (FF). Compared with the absorption spectrum of P13 thin film, P5 and P5a exhibit nearly overlapping absorption profiles in Fig. S4(b) (in ESI), revealing that relatively minor homocoupling defects barely alter the molecular aggregation behavior of the N2200 backbone.

To explore the charge recombination mechanisms of the corresponding devices, the dependence of V_{OC} on light intensity (P_{light}) was conducted, as depicted in Fig. S4(c) (in ESI). The relationship between V_{OC} and P_{light} can be expressed as $V_{\text{OC}} \propto (nkT/q)\ln(P_{\text{light}})$, where k is the Boltzmann constant, T is the thermodynamic temperature and q is the elementary charge.^[37–39] In comparison to the J52:P5a device (a slope of $1.845kT/q$), the slope ($1.766kT/q$) of the J52:P5 device is relatively smaller. These findings suggest that less trap-assisted recombination occurs in J52:P5 devices. As illustrated in Fig. S4(d) (in ESI), J_{SC} exhibits a power-law dependence on P_{light} following the relationship $J_{\text{SC}} \propto P_{\text{light}}^a$. The a values for both systems are close to 1, indicating negligible bimolecular recombination of the two systems.^[40] In addition, we evaluated the exciton dissociation probability at short circuit condition (P_{diss}) and charge collection probability at maximum output point (P_{coll}) by plotting the curves of photocurrent density (J_{ph}) versus effective voltage (V_{eff}) (Fig. S4e in ESI). P_{diss} and P_{coll} can be calculated *via* $J_{\text{SC}}/J_{\text{sat}}$ and $J_{\text{ph}}/J_{\text{sat}}$, respectively, where J_{sat} denotes the saturated photocurrent density obtained at $V_{\text{eff}}=4$ V. The P_{diss} and P_{coll} values of the J52:P5 device reach 98.2% and 83.7%, while those of the J52:P5a-based device are 97.5% and 80.5%. This result reveals that the J52:P5 device enables more efficient exciton dissociation at the donor-acceptor interface compared with the J52:P5a counterpart. In summary, the J52:P5 device exhibits the most favorable carrier dynamics, which contributes to the pronouncedly enhanced FF of the corresponding device.

Given the distinct difference in open-circuit voltage (V_{OC}) between P5-based ($V_{\text{OC}}=0.790$ V) and P5a-based ($V_{\text{OC}}=0.742$ V) devices, and considering that non-radiative loss is a domi-

nant factor governing the V_{OC} of organic photovoltaic (OPV) devices,^[41] we performed electroluminescence external quantum efficiency (EQE_{EL}) measurements. As presented in Fig. S4(f) (in ESI), possibly due to the influence of high defect density within the devices, both types of devices exhibit electroluminescence quantum efficiencies that are difficult to bring to saturation, although the J52:P5-based device exhibits substantially higher EQE_{EL} values across the entire measurement range relative to the J52:P5a counterpart. This observation verifies that the J52:P5 device suffers from suppressed non-radiative energy loss, which accounts for its elevated V_{OC} of 0.790 V.

Collectively, these results verify that a lower fraction of homocoupling fragment can suppress charge recombination as well as non-radiative energy losses, simultaneously boosting FF and V_{OC} of the corresponding photovoltaic devices.

CONCLUSIONS

This work successfully developed a highly efficient and universally applicable RT Stille polymerization system, which effectively addresses the critical issue of homocoupling defects in traditional thermally activated Stille polymerization. Its broad substrate universality was verified by the successful synthesis of various D-A type conjugated polymers, including classic photovoltaic materials (J60, PBDB-T, PM6, N2200), dye-based polymers, and random terpolymers. Defect analysis confirmed that the system could significantly suppress homocoupling of both electrophilic and nucleophilic monomers, and photovoltaic device tests demonstrated that polymers (J60, PBDB-T, N2200, PNDI-TVt) synthesized *via* this system exhibit enhanced PCEs. Further physical characterizations of the photovoltaic devices confirm that a lower fraction of homocoupling fragments can suppress charge recombination as well as non-radiative energy losses. This research enriches the methodology of RT Stille polymerization, provides a reliable synthetic strategy for preparing low-defect, high-performance conjugated polymers, and offers guidance for the development and large-scale preparation of organic optoelectronic materials.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-026-3826-z>.

Data Availability Statement

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

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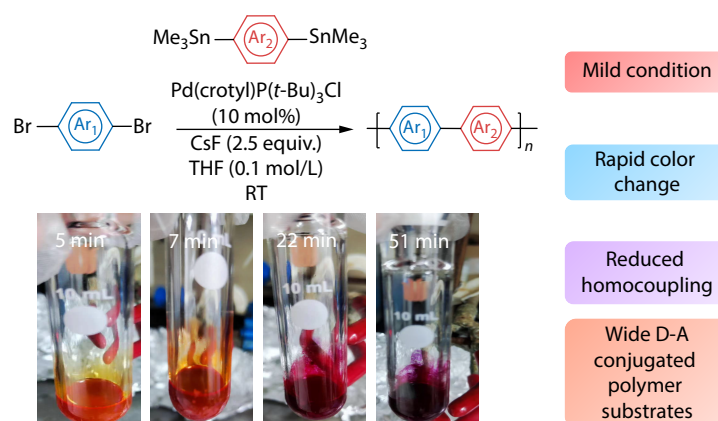
Graphical Abstract

An Efficient Catalytic System for Room-temperature Stille Polymerization

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This work establishes a CsF-assisted room-temperature Stille polymerization system with $\text{P}(\text{t-Bu}_3)\text{Pd}(\text{crotyl})\text{Cl}$ precatalyst, which suppresses homocoupling defects and exhibits broad substrate scope to afford diverse donor-acceptor (D-A) conjugated polymers for organic photovoltaic (OPV) and organic electronics.



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