An Efficient Precatalyst Approach for the Synthesis of Thiazole-Containing Conjugated Polymers via Cu-Catalyzed Direct Arylation Polymerization (Cu-DArP)

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ABSTRACT: Over the past decade, direct arylation polymerization (DArP) has emerged as a facile and sustainable methodology for the synthesis of conjugated polymers. Recently, we developed Cu-catalyzed DArP (Cu-DArP) as a low-cost, Pd-free synthetic pathway, which enables conjugated polymers to be synthesized with high molecular weights and minimization of defects. However, the lack of study on the use of Cu-precatalysts in small-molecule direct arylation poses significant limitations for Cu-DArP to potentially overtake conventional Pd-catalyzed methodology, such as the low solubility and stability of the previously employed CuI. Therefore, in this report, we decide to explore the utility of a well-defined, easy-to-prepare, highly-soluble and stable precatalyst, Cu(phen)(PPh$_3$)Br, as an alternative to the CuI, 1,10-phenanthroline catalytic system previously used for Cu-DArP. Herein, we report a drastic improvement of Cu-DArP methodology for the synthesis of 5,5'-bithiazole (5-BTz)-based conjugated polymers enabled by an efficient precatalyst approach, affording polymers with good M$_n$ (up to 16.5 kDa) and excellent yields (up to 79%). ^{1}HNMR studies reveal the exclusion of homo-coupling defects, which further verifies the excellent stability of Cu(phen)(PPh$_3$)Br compared to CuI. Furthermore, we were able to decrease the catalyst loading from 15 mol% to only 5 mol% (M$_n$ of 11.8 kDa, 64% yield), which is unprecedented when aryl-bromides are employed for Cu-DArP. Significantly, 5-BTz was shown to be inactive under various of Pd-DArP conditions, which demonstrates the high compatibility of Cu-DArP as the only pathway for the C-H activation of the 5-BTz unit and a clear case demonstrating an advantage of Cu-DArP relative to Pd-DArP.

For decades, conjugated polymers have been explored as an effective class of materials for a wide-range of applications such as organic photovoltaics (OPVs), organic light-emitting diodes (OLEDs), organic field effect transistors (OFETs), chemical sensors, and bioelectronics.[1–5] In recent years, Direct arylation Polymerization (DArP) has been found to provide a facile and environmentally-benign pathway for conjugated polymer synthesis by eliminating the need for toxic tin- or boron-functionalized monomers.[6–11] However, current DArP methodologies are reliant on catalysis by Pd, which is 4000 times less earth-abundant and 16 times more expensive in comparison to Cu.[12] To address this important issue of sustainability in DArP, we developed the first Cu-catalyzed DArP (Cu-DArP) conditions that allowed conjugated polymers to be prepared with high molecular weights (M$_n$ up to 24.5 kDa) and minimized homo-couplings or branching defects.[13–15] Through careful optimization of reaction conditions, we were able to lower the Cu-catalyst loading and successfully employ aryl-bromides in place of the less stable and more expensive aryl-iodides, significantly improving and practicality of Cu-DArP towards the replacement of Pd-catalysts.[15]

However, unlike Pd-catalyzed protocols, which have been extensively studied to employ stable, efficient Pd-complexes as precatalysts such as Pd$_2$(dba)$_3$, PdCl$_2$(PPh$_3$)$_2$, and Pd-(Herann-Beller) (Figure 1a),[16] the use of Cu-precatalysts in Cu-catalyzed small molecule direct arylation has not been reported to the best of our knowledge.[17] Pioneering studies in the field led by Daugulis et al., Miura et al., and You et al. utilized CuI as catalyst and phenanthroline or PPh$_3$ as ligand without any use of Cu-precatalysts.[18–21] When transcribing such conditions to polymerization methodology, the nature

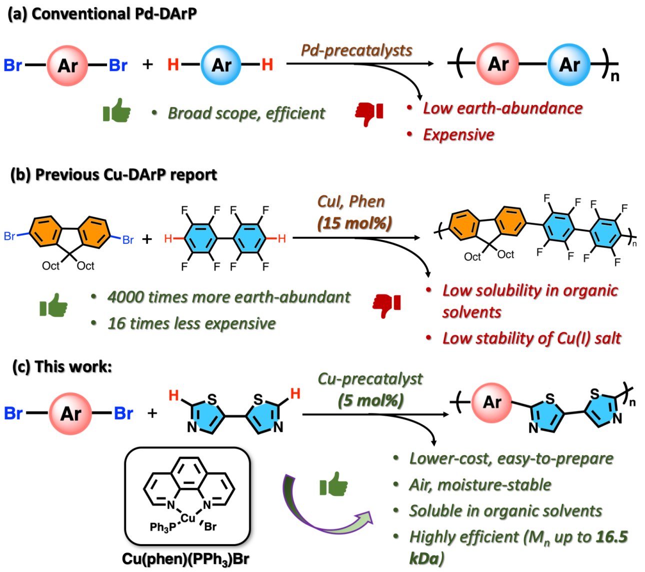


Figure 1. Summary of Pd-DArP and Cu-DArP development.

of CuI as an inorganic salt exhibits certain drawbacks, which hinder Cu-DArP from potentially overtaking conventional Pd-catalyzed methodologies (Figure 1b). First, Cu(I) salts display low solubility in organic solvents,[17] which likely leads to the need for polar amide solvents (such as N, N-dimethylacetamide, i.e. DMA) in our previous reports.[13-15] Another drawback is the low stability of Cu(I) salts under the harsh conditions required for Cu-DArP (140 °C),[17] which agrees with our experimental observations that green inorganic salts were formed after polymerizations in our previous studies (likely Cu(II) salts).[13-15] These major drawbacks of Cu(I) salts previously adapted for Cu-DArP may have resulted in undesired side reactions and the need for higher Cu-catalyst loadings in our reports, especially when aryl-bromides were employed (15-50 mol%).[15] Considering that the employment of Pd-precatalysts in Pd-catalyzed DArP has contributed considerably the development of the field, we envisioned the use of a well-defined, soluble, and stable Cu-precatalyst could enable us to access a more effective and versatile Cu-DArP methodology.

Cu(phen)(PPh$_3$)Br, is a chemically well-defined Cu(I) complex (Figure 1c), that was first synthesized and employed by Venkataraman et al. as a highly efficient Cu-precatalyst for the formation of aryl-nitrogen, aryl-oxygen, and aryl-carbon bonds.[22] However, the use of Cu(phen)(PPh$_3$)Br in biaryl coupling reactions has not been reported to the best of our knowledge. It can be readily prepared simply by the addition of 1,10-phenanthroline (phen) ligand to a solution of tris(triphenylphosphine) copper (I) bromide. This Cu-precatalyst has been shown to display excellent stability in air and moisture, and is highly soluble in common organic solvents.[22] Additionally, Cu(phen)(PPh$_3$)Br exhibits high structural resemblance to our previous Cu-DArP catalytic system (CuI, phen). Therefore, we identified Cu(phen)(PPh$_3$)Br as an ideal candidate for the further pursuit of our Cu-DArP studies.

While our previous Cu-DArP studies focused on fluorinated monomers such as 2,2′,3,3′,5,5′,6,6′-octafluoro-4,4′-diphenylene,[14,15] we turned our attention to thiazole-containing conjugated polymers due to their prevalence in organic electronics.[23] Specifically, electron-deficient bithiazole (BTz)-based conjugated polymers display improved charge-transport properties and stability in a variety of applications owing to their low highest occupied molecular orbital (HOMO) levels.[24] Furthermore, due to the reduced steric hinderance between repeating units and strong intermolecular S-N interactions, BTz units afford Donor-Acceptor (D-A) copolymers with more planar backbones and higher degrees of crystallinity.[25] Therefore, BTz units such as 2,2’-bithiazole (2-BTz) and 5,5’-bithiazole (5-BTz) have been proven to be attractive building blocks for materials applied in OPVs and OFETs.[23,25,26]

However, while numerous reports have demonstrated highly effective Pd-DArP conditions for the synthesis of 2-BTz copolymers,[27–29] the regio-isomeric 5-BTz unit is reported to be surprisingly inactive under a variety of Pd-DArP protocols by Sommer et al. (Figure 2a).[29] Although Kanbara et al. successfully activated the C-H bonds at the C-2 position of the thiazole unit via Cu-catalyzed oxidative direct arylation polymerization (oxi-DArP), the resulting polymeric outcomes are identical to 2-BTz copolymers synthesized via Pd-DArP (Figure 2a).[30] To the best of our knowledge, the 5-BTz monomer has not been polymerized via DArP, presumably due to the lack of catalytic activity of Pd towards the C-H bond at the C-2 position.

Our research in the literature of small-molecule direct arylation studies reveals a similar reactivity pattern of the thiazole unit (Figure 2b). While Pd-catalysts are highly regioselective towards C-5 arylation due to a lower activation energy barrier (23.7 kcal mol^{-1} vs. 26.3 kcal mol^{-1} (C-2), respectively),[31,32] C-2 arylation is selectively preferred when Cu(I) catalysts or Pd/Cu(I) co-catalytic systems are applied.[18,33] This behavior can be explained by the strong Cu(I)-coordination from the N-3 site, which increases the acidity of the C-H bond at the C-2 position.[31] Operating under this hypothesis, we were emboldened to pursue Cu-DArP as potentially the only methodology to access the C-H activation of the 5-BTz monomer (Scheme 1). Herein, we present the first 5-BTz copolymer, poly[(9,9-bis(2-ethylhexyl)fluorene-2,7-diyl)-alt-(5,5’-bithiazole)] (PF-5BTz), synthesized with high M_n and yields via Cu-DArP using a robust Cu-precatalyst approach.

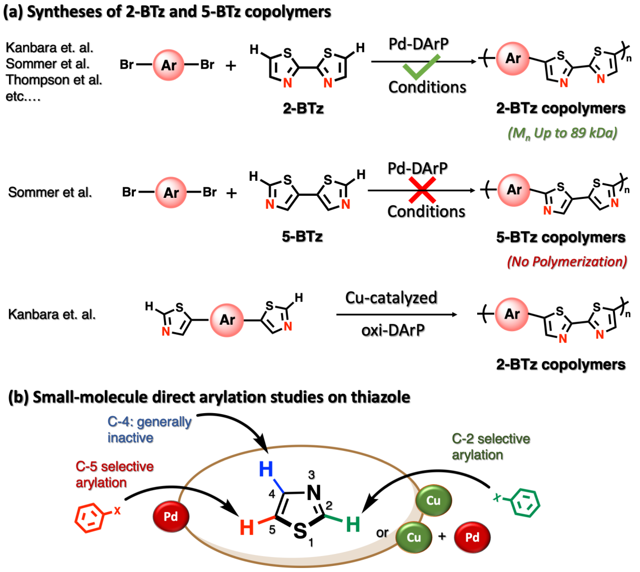
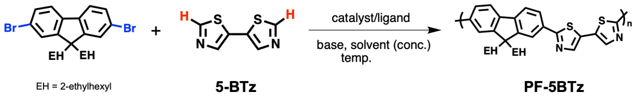


Figure 2. (a) Summary of different polymerization methods for BTz-containing conjugated polymers; (b) Summary of small-molecule selective direct arylation on thiazole unit.

As shown in Scheme 1, 2,7-dibromo-9,9-bis(2-ethylhexyl)-9*H*-fluorene was selected as a coupling partner to 5-BTz for our model study. Detailed description for the synthesis of Cu-precatalysts, monomers, and polymers can be found in the Supporting Information (SI). A DMA/m-xylene (1:1) co-solvent system was used based on our previous report, which demonstrated that it is critical for Cu-DArP to proceed using aryl-bromides.[15] Daugulis et al. reported that the C-2 position of thiazole can be arylated with high yields using CuI, phen as the catalytic system and K_3PO_4



Scheme 1. Synthesis of PF-5BTz using 2,7-dibromo-9,9-bis(2-ethylhexyl)fluorene and 5-BTz (Conditions listed in Table 1).

Table 1. Cu-DArP conditions for the synthesis of PF-5BTz and polymerization results.

entry	catalyst/ligand[a]	cat. mol %	Base[b]	solvent[c] (conc.)	temp. (°C)	time (hr.)	M_n (kDa)[d], Đ[d]	yield[d] (%)
1[e]	CuI/phen	15	K_3PO_4	DMA/m-xylene (0.4 M)	140	72	-	0
2[e]	CuI/phen	15	tBuOLi	DMA/m-xylene (0.4 M)	140	72	-	0
3[e]	CuI/phen	15	K_2CO_3	DMA/m-xylene (0.4 M)	140	72	3.8, 1.5	36
4	Cu(phen)(PPh$_3$)Br	15	K_2CO_3	DMA/m-xylene (0.4 M)	140	16	16.5, 1.6	79
5	Cu(phen)(PPh$_3$)Br	15	K_2CO_3	DMA/m-xylene (0.2 M)	140	72	13.1, 1.7	65
6	Cu(neocup)(PPh$_3$)Br	15	K_2CO_3	DMA/m-xylene (0.4 M)	140	16	-	0
7	Cu(bipy)(PPh$_3$)Br	15	K_2CO_3	DMA/m-xylene (0.4 M)	140	16	-	0
8	Cu(phen)(PPh$_3$)I	15	K_2CO_3	DMA/m-xylene (0.4 M)	140	16	3.2, 1.7	29
9	Cu(phen)(PPh$_3$)Br	5	K_2CO_3	DMA/m-xylene (0.4 M)	140	16	11.8, 1.8	64
10	Cu(phen)(PPh$_3$)Br	5	K_2CO_3	m-xylene (0.4 M)	140	16	-	0
11[f]	Cu(phen)(PPh$_3$)Br	5	K_2CO_3	DMA/m-xylene (0.4 M)	140	16	-	0
12[g]	Pd(OAc)$_2$	2	K_2CO_3	DMA (0.04 M)	70	16	-	0
13[h]	Pd$_2$(dba)$_3$/P(o-anisyl)$_3$	1	Cs_2CO_3	THF (0.2 M)	120	16	-	0
14[h]	PdCl$_2$(PPh$_3$)$_2$/ P(o-anisyl)$_3$	2	Cs_2CO_3	CPME (0.2 M)	110	16	-	0

[a]For CuI, 99.999%-Puratrem Cu(I) iodide was used. phen = 1,10-Phenanthroline. neocup = Neocuproine. bipy = 2,2'-Bipyridine. [b]All Cu-DArP (entries 1-10) were conducted using 4 equivalence of base. All Pd-DArP (entries 11-13) were conducted using 3 equivalence of base. [c]DMA = N,N-dimethylacetamide. THF = Tetrahydrofuran. CPME = Cyclopentyl methyl ether. [d]Determined for polymer products after purification. [e]Ligand loadings were 1:1 ratio to Cu(I) iodide. [f]2-BTz was used instead of 5-BTz. [g]0.3 equiv. of neodeconoic acid was used as an additive. [h]Ligand loadings were 2:1 ratio to Pd-catalysts. 0.5 equiv. of neodeconoic acid was used as an additive.

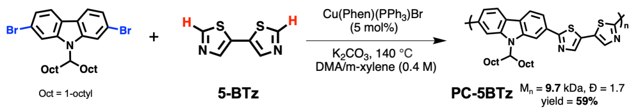
or tBuOLi as base.[18,19] However, desired polymerizations did not proceed under either conditions (Table 1, entry 1, 2), contrasting our previous reports in which K_3PO_4 provides the optimal conditions for Cu-DArP.[14,15] After changing the base to a milder base, K_2CO_3, while keeping the same catalytic system (15 mol% CuI, phen), PF-5BTz was afforded with M_n of 3.8 kDa and a low yield (36%) (entry 3). ^{1}HNMR reveals a significant amount of acceptor-acceptor homocoupling (α) (detailed discussion is provided below), potentially due to the oxidative thiazole (C-H)/thiazole (C-H) coupling catalyzed by Cu(II), as reported by Kanbara et al.[30] This illustrates the instability of the CuI, phen catalytic system, which is prone to oxidation to form Cu(II).[17] Remarkably, switching the Cu-catalyst to the aforementioned bench-stable, soluble Cu-precatalyst, Cu(phen)(PPh$_3$)Br, drastically improved the efficiency of the polymerization while keeping the same catalyst loading (15 mol%), affording PF-5BTz with an excellent M_n (16.5 kDa) and a good yield (79%) in only 16 hours (entry 4). ^{1}HNMR confirms no sign of α homocoupling, which is likely a result of an improved stability of Cu(phen)(PPh$_3$)Br, providing a stable Cu(I) source. By comparison with entry 3, this result further verifies reports by Venkataraman et al. that Cu(phen)(PPh$_3$)Br is a highly efficient, stable and soluble Cu-precatalyst for Pd-free cross-coupling chemistry.[22] Decreasing the concentration of the polymerization while prolonging the reaction time to 72 hours did not improve the M_n or yield (13.1 kDa, 65%, respectively) (entry 5).

Venkataraman et al. also reported two analogous Cu-precatalysts, Cu(neocup)(PPh$_3$)Br and Cu(bipy)(PPh$_3$)Br, which can be prepared in the same fashion as Cu(phen)(PPh$_3$)Br (see SI for detailed synthesis of Cu-precatalysts).[22] These species were also found to be robust in catalyzing cross-coupling reactions such as the formation of aryl-nitrogen and aryl-oxygen bonds.[22] Despite the suppression of the desired polymerization found utilizing these two Cu-precatalysts (entry 6, 7), the ease of structural modification of Cu(phen)(PPh$_3$)Br can potentially impact the future development of Cu-DArP. This is in agreement with report by You et al. that phen is the most effective bidentate pyridinic ligand for Cu-catalyzed direct arylation.[21] Additionally, we synthesized the iodo-counterpart of the Cu-precatalyst, Cu(phen)(PPh$_3$)I, which afforded PF-5BTz with a much lower M_n (3.2 kDa) and yield (29%), accompanied by the visible decomposition of the precatalyst (entry 8). By comparison, this demonstrates the thermal stability of Cu(phen)(PPh$_3$)Br, even under relatively harsh condition (140 °C).

Subsequently, with the optimal condition (entry 4) in hand for 15 mol% catalyst loading, we decided to probe a lower catalyst loading of 5 mol%, which afforded PF-5BTz with a good M_n of 11.8 kDa and a yield of 64% (entry 9). This result marks the first conjugated polymer synthesized by DArP using only 5 mol% of Cu-catalyst when an aryl-bromide is used as the coupling partner, which has significantly improved upon our previously disclosed Cu-DArP report.[15] Next, we were interested to investigate the potential of using non-polar solvents such as m-xylene for the newly-developed Cu-DArP protocol without the use of an amide solvent (DMA), since Cu(phen)(PPh$_3$)Br was found to be soluble in common organic solvents, such as toluene.[22] However, no polymer product was obtained, although oligomers likely formed based on an observed color change (entry 10). This result indicates that the role of DMA in Cu-DArP may not be limited to the improvement of the solubility of Cu-catalysts. DMA has been demonstrated to form Pd-complexes and serve as a critical component of the Pd catalytic system.[34] Similarly, DMA also likely facilitates Cu-DArP by playing a similar role as a ligand to form DMA-Cu(I)-complexes during the catalytic cycle. A control experiment was then performed by replacing the 5-BTz unit with a 2-BTz monomer, which completely inhibited the polymerization (entry 11). By comparison, a conclusion can be drawn that Cu-DArP conditions preferably activate the C-2 positions of the 5-BTz unit, as opposed to their inability to activate the C-5 positions of the 2-BTz unit, which is in agreement with small-molecule studies (Figure 2b).[18,31]

Having achieved an unprecedented 5-BTz copolymer synthesis via DArP using a Cu-precatalyst strategy, we were intrigued to further confirm the inactivity of the 5-BTz monomer under Pd-DArP protocols, as reported by Sommer et al.[29] Three different Pd-DArP conditions were attempted for the synthesis of PF-5BTz (entry 12-14). The selected conditions have been proven to be versatile to afford a variety of conjugated polymer structures, including homo-polymers and D-A copolymers with minimal homo-couplings or defects using different Pd-catalysts.[10,12] Interestingly, no polymer product was obtained when these Pd-DArP conditions were employed (entry 12-14). These results verify our assumption that the C-H activation of the 5-BTz monomer unit can only be achieved by Cu-catalysts, which is a significant step forward for Cu-DArP to potentially rival Pd-catalyzed methodology.

Finally, to probe the scope of the developed Cu-DArP method, we turned our focus to the synthesis of a carbazole-containing conjugated polymer, poly[(N-9'-heptadecanyl-2,7-carbazole)-alt-(5,5'-bithiazole)] (PC-5BTz) (Scheme 2). By using only 5 mol% of Cu(phen)(PPh$_3$)Br, PC-5BTz was afforded with a moderate M$_n$ of 9.7 kDa and yield of 59%. Taking into account that a 9-heptadecyl side-chain was used instead of the more soluble bis(2-ethylhexyl) side-chain in PF-5BTz, we presumed a lower solubility of PC-5BTz was the main reason for a slightly lower M$_n$ and yield.



Scheme 2. Synthesis of PC-5BTz.

^{1}HNMR spectroscopy studies were performed to characterize and confirm the proposed polymer structures. All recorded ^{1}HNMR data for Table 1 and Scheme 2 is available in the SI. Figure 3 shows detailed peak-assignments, including end-group and defect analyses of two representative polymers (PF-5BTz) synthesized using Cu(phen)(PPh$_3$)Br (Table 1, entry 4) and CuI, phen employed in our previous reports (Table 1, entry 3).[13–15] The major resonances of PF-5BTz match with that previously synthesized via Pd-catalyzed oxi-DArP with resonances centered at δ8.02 and δ7.84 (ppm).[35] The integration ratio of these major resonances can be accurately assigned to protons of PF-5BTz repeat unit (see Figure S8-S11 in the SI). This indicates the absence of branching and cross-linking defects embedding in the polymer structure, according to a report by Kanbara et al.[30] The assignments of end groups were performed by comparing the collected PF-5BTz spectra to those of model compounds with similar structures.[35] α homo-coupling was assigned by comparing the ^{1}HNMR spectra of PF-5BTz to a BTz-based homo-polymer.[36,37] A detailed discussion regarding these assignments can also be found in the SI (see section 8 of SI and Figure S13).

Importantly, as shown in Figure 3a, PF-5BTz synthesized via the newly-developed Cu-precatalyst approach (entry 4) display the absence of an α homo-coupling signal, which would be expected if a Cu(II) species were generated during the reaction based on the report by Kanbara et al.[30] This result suggest Cu(phen)(PPh$_3$)Br as a highly robust precatalyst to provide a stable Cu(I) source, preventing oxidation to Cu(II) from occurring. The addition of a PPh$_3$ ligand to the Cu-catalyst structure likely improves the oxidative stability of Cu(I), since similar behavior of phosphine ligands has been reported to stabilize Pd(0)/Pd(II) species in cross coupling reactions.[38] By comparison, PF-5BTz prepared using the previous Cu-DArP methodology (entry 3) exhibits a significant amount of α homo-coupling defect (δ7.96) (Figure 3b). Furthermore, the absence of the terminal 5-BTz end-groups (d, d', e), a low M$_n$(3.8 kDa), and a significant amount of the fluorene end-groups (a-c') indicate the presence of the thiazole (C-H)-thiazole (C-H) oxidative coupling, likely

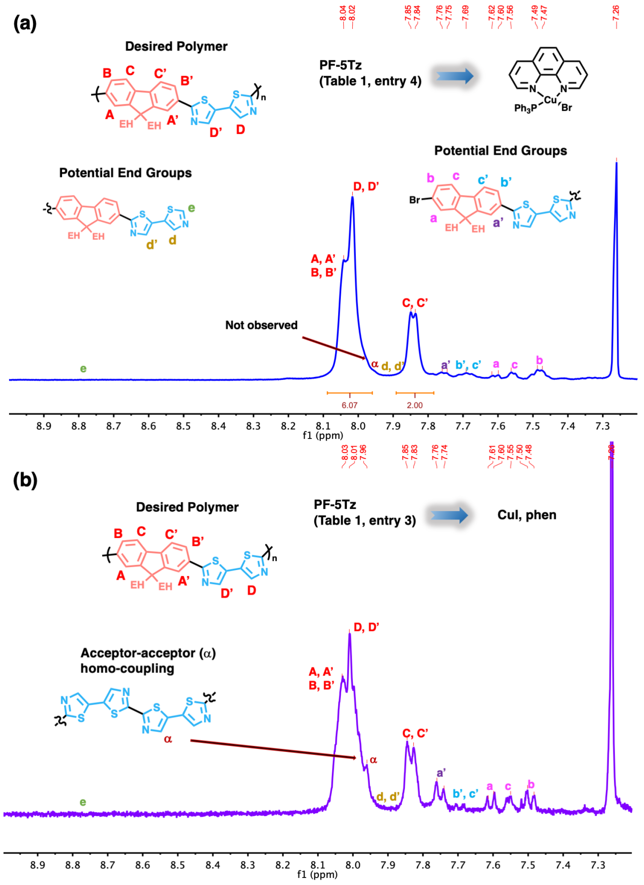


Figure 3. ^{1}HNMR analyses of representative polymers: (a) PF-5BTz (Table 1, entry 4) synthesized using Cu(phen)(PPh$_3$)Br and (b) PF-5BTz (Table 1, entry 3) synthesized using CuI, phen. Potential resonances for end groups and defects are denoted. α = acceptor-acceptor homocoupling (δ7.96). Collected in CDCl$_3$ at 25 °C and 500 MHz.

catalyzed by Cu(II) generated from an unstable Cu(I) source (CuI).[30]

In summary, a novel precatalyst approach for Cu-DArP methodology has been presented, which allows for a drastic improvement for the synthesis of PF-5BTz. By replacing our previously reported CuI, phen catalytic system with an easy-to-prepare, soluble, and stable Cu-precatalyst, Cu(phen)(PPh_3)Br, the M_n of PF-5BTz was substantially improved from 3.8 kDa to 16.5 kDa with a yield increased from 36% to 79%. Structural analysis using ^{1}HNMR spectroscopy reveals the absence of α homo-coupling when Cu(phen)(PPh_3)Br was used, suggesting it as a highly stable Cu(I) source compared to CuI. This newly-developed Cu-DArP condition allows a decrease of Cu-catalyst loading from 15 mol% to 5 mol% to afford PF-5BTz with a good M_n of 11.8 kDa and a yield of 64%, which is the lowest when aryl-bromides were employed. Impressively, Cu-DArP was demonstrated as the only methodology to achieve the C-H activation of the 5-BTz unit, since the synthesis of PF-5BTz under various of Pd-DArP conditions were proven unsuccessful, which is in agreement with literature reports including polymer syntheses as well as small molecule studies. These results also demonstrate a clear example of a case where Cu-DArP proves more effective than Pd-DArP. Future work will focus on designing new Cu-precatalysts and further optimizing polymerization conditions to seek a broader substrate scope.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures including the synthesis and characterization for all monomers, polymers and Cu-precatalysts are included in the supporting information (SI). This material is available free of charge via the internet at http://pubs.acs.org.

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