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Metal-Free, Multicomponent Synthesis of Pyrrole-Based π-Conjugated Polymers from Imines, Acid Chlorides, and Alkynes

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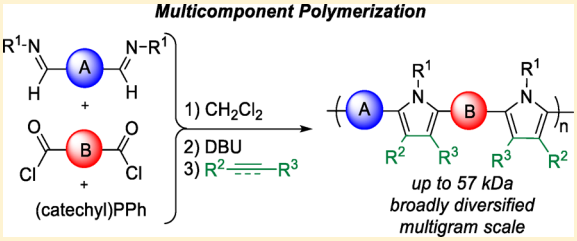
Supporting Information

ABSTRACT: Multicomponent coupling reactions (MCRs) are becoming increasingly used in the synthesis of macromolecules, as they can allow the rapid generation of libraries of materials as a method to tune properties. MCRs could prove particularly useful in the synthesis of π-conjugated polymers in which structural changes are necessary for fine-tuning of electronic properties. We describe here the first metal-free multicomponent approach to conjugated polymers. This reaction exploits the coupling of imines, acid chlorides, and (catechyl)PPh to generate phospha-münchnone-containing polymers, which can be converted to poly(pyrroles) via cycloaddition. The platform allows for the efficient synthesis of families of high molecular weight polymers in one step from readily available monomers.



INTRODUCTION

Multicomponent coupling reactions (MCRs) have gained utility in synthetic chemistry.[1] In contrast to the more traditional multistep assembly of products, MCRs provide the potential to directly generate complex structures from three or more building blocks, often with minimal waste and with direct access to structural diversity. While these reactions have been most heavily exploited in small molecule organic synthesis and the generation of compound libraries of relevance to pharmaceutical development, the application of MCRs to polymer synthesis has also recently begun to attract attention.[2] Important examples include the assembly of ester- or amide-containing polymers via the use of Passerini[3] and Ugi[4] three- and four-component reactions, "click"-inspired reactions such as the Cu-catalyzed three-component synthesis of polyamidines,[5] mercaptoacetic acid locking imine (MALI),[6] A^3-coupling reactions,[7] and others.[8] Due to their high efficiency, MCRs have also been used in postpolymerization functionalization[9] and in the synthesis of sequence-defined macromolecules.[10]

One area where multicomponent polymerization reactions could prove of significant utility is in the construction of π-conjugated polymers. Conjugated polymers have emerged as useful materials for a range of electronic applications (e.g., light-emitting devices, photovoltaics, field effect transistors, molecular sensors, charge transport, and others).[11] An important feature of conjugated macromolecules is their tunability, where changes to their structure or substituents can be used to create finely tuned polymers. While effective as a design tool, exploiting this tunability often results in structurally complex compounds and can therefore present synthetic challenges. Conjugated polymers generally incorporate complexity from the monomer(s), which themselves require a multistep synthesis.[12] This can make access to the structural diversity to optimize properties an iterative sequence where each repeat unit must be synthesized prior to polymerization. Interestingly, despite the useful features of multicomponent polymerizations, only a few examples of the application of this technology to conjugated polymers have been reported. In early examples, Endo and Tomita described the use of multicomponent palladium-catalyzed cross-coupling reactions to prepare alternating conjugated polymers (e.g., Figure 1a).[13,14] Tang and coworkers have reported one-pot tandem three-component polymerizations for the synthesis of cross-conjugated polymers (e.g., Figure 1b).[15,16] Recently, we have noted that structurally more complex and fully conjugated units can be assembled at the same time as the polymer in the palladium-catalyzed multicomponent formation of pyrrole-based conjugated polymers (Figure 1c).[17] However, one limitation of these multicomponent methods relative to more classic approaches to poly-heteroaromatics is their often high substrate specificity and poor diversity (e.g., the required use of fluorenyl imines in Figure 1c), as well as their reliance upon palladium catalysis, which can be sensitive to perform and can require efforts to remove palladium from the product (to minimize its influence on properties). In addition, as with many multicomponent polymerizations, the molecular weights observed to date in fully conjugated polymer synthesis are often moderate (often <15 repeat units); presumably reflecting the challenge of designing a reaction with sufficient efficiency to generate high molecular weight materials.

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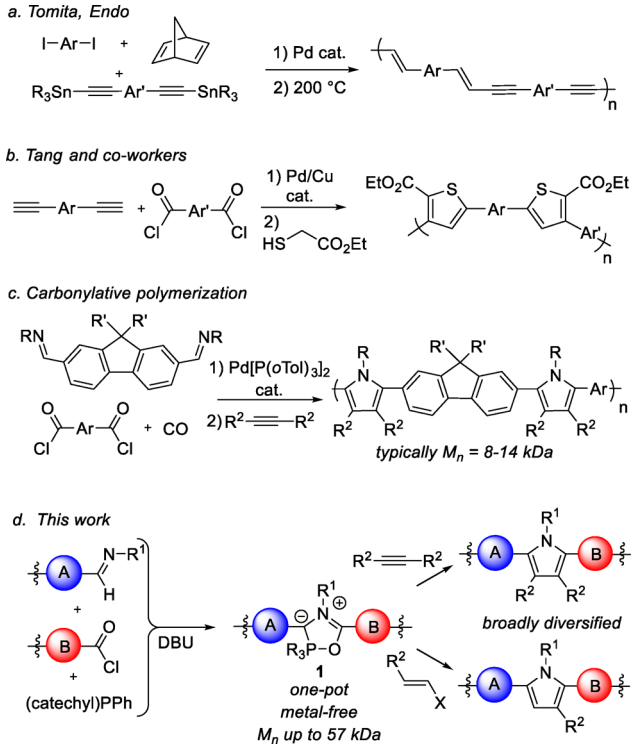


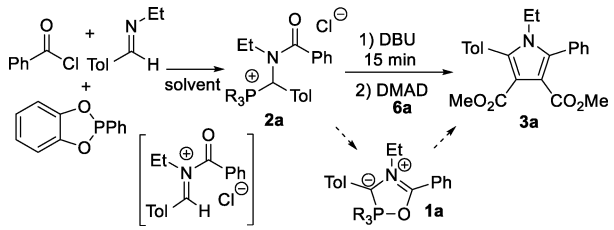
Figure 1. Multicomponent conjugated polymer synthesis.

In considering these issues, we have become interested in the design of a more broadly applicable multicomponent polymerization reaction. To do so, we hoped to incorporate a number of key features, including that it (a) employs combinations of available substrates, (b) is straightforward to implement, (c) can be diversified, (d) does not use palladium catalysis, and importantly, (e) can allow the reliable synthesis of high molecular weight conjugated polymers. In this regard, we have recently reported a new small molecule coupling reaction of imines, acid chlorides, and (catechyl)PPh to generate 1,3-dipoles **1** (Figure 1d), i.e., phospha-münchnones.[18] Compound **1** can undergo 1,3-dipolar cycloaddition with dipolarophiles such as alkynes to generate polysubstituted pyrroles. A feature of this reaction for a polymerization is its synthetic simplicity, as it is a condensation of stable materials, each of which can potentially arise from commodity substrates (dialdehydes, diacid chlorides, alkynes, or alkenes). As such, provided the efficiency of this transformation is sufficient for a polymerization, this could provide an attractive platform to assemble conjugated polymers. We report below our studies toward this goal. These demonstrate that the formation of poly-**1** can open a new, metal-free route to construct conjugated materials from multiple monomers. This polymerization is easily performed, scalable, proceeds in high molecular weights, and can allow the buildup of broad families of conjugated polymers by simple variation of the three available substrates.

■ RESULTS AND DISCUSSION

Stoichiometric Model Reactions. The coupling of imine, acid chloride, (catechyl)PPh, and base followed by alkyne has been previously reported to generate pyrroles in good yields (ca. 80%), though not in sufficient so to form high molecular weight polymers.[18a] Thus, prior to examination of this reaction for polymerizations, we first probed more closely the efficiency of the small molecule coupling reaction. As illustrated in Table 1, monitoring this reaction by in situ ^{1}H NMR analysis ($CDCl_3$) shows the formation of phosphonium salt **2a** in 93%

Table 1. Optimization of Multicomponent Reaction[a]



entry	solvent	2a (%)	1a (%)	3a (%)
1	$CDCl_3$	93 (9 h)	88[b]	58
2	C_6D_6	insoluble	78	61
3	CD_2Cl_2	99 (5 h)	98	82
4	CD_3CN	98 (3 h)	97	75
5	CD_2Cl_2	99 (5 h)	92[c]	92
6	CD_2Cl_2[d]	99 (5 h)	98	99[e]

[a]Conditions: imine (15 mg, 0.10 mmol), PhCOCl (14 mg, 0.10 mmol), (catechyl)PPh (24 mg 0.11 mmol). **1a**: DBU (18 mg, 0.12 mmol), 15 min. **3a**: DMAD (43 mg, 0.3 mmol). [b]0.2 mmol DBU. [c]0.105 mmol DBU. [d]**1a** precipitated before DMAD addition. [e]From **1a**.

yield (entry 1). The addition of DBU base results in the formation of the 1,3-dipole **1a**, but it requires the use of a large excess of base and is still incomplete. Cycloaddition with dimethylacetylene dicarboxylate (DMAD **6a**) forms pyrrole in poor yield (58%). We postulated that the yield and reactivity of the ionic intermediates in this reaction (e.g., **1a**, **2a**) may show a strong dependence on solvent polarity. For example, performing this reaction in less polar benzene results in the incomplete disappearance of the reagents and the formation of **2a** as an insoluble precipitate (entry 2). Conversely, more polar solvents result in the essentially quantitative formation of **2a** and phospha-münchnone **1a** (entries 3 and 4), although in this case the 1,3-dipole is insoluble in acetonitrile. Only moderate yields of pyrrole are again observed upon DMAD cycloaddition in either solvent. Control experiments demonstrate that this arises in part from side reactions between the alkyne and the excess DBU employed to fully form **1a**. While this effect can be minimized by the use of a stoichiometric amount of DBU base (92%, entry 5), a more straightforward solution is to exploit the insolubility of **1a** in acetonitrile, which can allow its facile removal from the reaction mixture by precipitation, and upon subsequent alkyne addition to **1a** forms pyrrole in quantitative yields (entry 6). Notably, ^{1}H and ^{31}P NMR analysis (Figures S1 and S2) shows no evidence for byproducts in any of these steps, suggesting that this should be a viable platform for a polymerization.

Polymerization Chemistry. With the model reaction in hand, we next examined the ability of this chemistry to generate conjugated polymers. To do so, four reagents were employed: terephthaloyl chloride **5a**, diimine **4a** derived from terephthaldehyde, (catechyl)PPh, and dimethyl acetylenedicarboxylate (**6a**). The analogous reaction to that performed with model compounds above leads to the formation of the polymer **7a** in only moderate molecular weight (4.8 kDa, Table 2, entry 1). Since the molecular weight of the polymer is set during the addition of phosphine to the equilibrium generated poly(iminium salt), increasing solvent polarity (entry 2)[19] or

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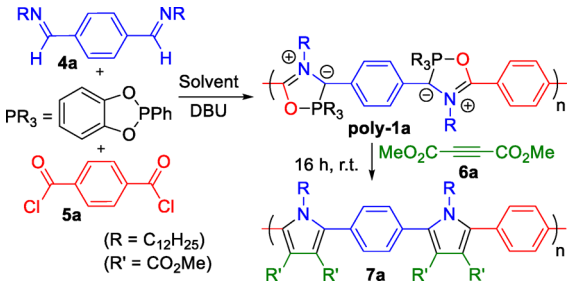
Table 2. Multicomponent Polymerization[a]



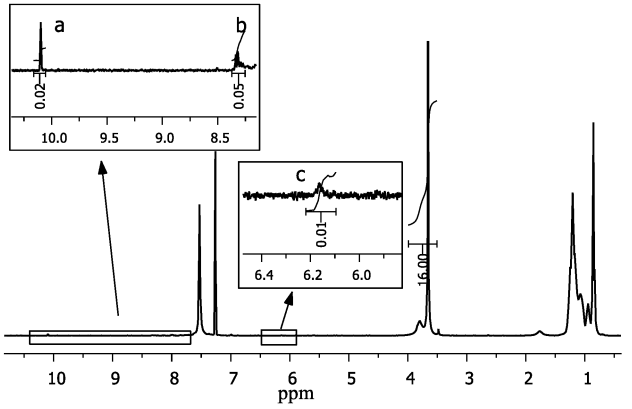
entry	solvent	temp (°C)	yield[b] (%)	M_n (kDa)/PDI
1	CH_2Cl_2	rt	71	4.8/1.6
2	CH_2Cl_2:CH_3CN	rt	68	8.9/1.5
3	CH_3CN	rt	insoluble	
4	CH_2Cl_2	45	74	9.4/1.9
5	CH_2Cl_2	55	74	14.9/1.9
6	CH_2Cl_2:CH_3CN	55	75	15.0/2.3 (51.1)[c]

[a]Conditions: **4a** (47 mg, 0.10 mmol), **5a** (20 mg, 0.10 mmol), (catechyl)PPh (52 mg, 0.24 mmol), 0.6 mL of solvent, 24 h, then DBU (46 mg, 0.30 mmol). **1a** precipitated with CH_3CN. **6a** (43 mg, 0.30 mmol). [b]Isolated yield of **7a** after precipitation in methanol.[21] [c]Absolute M_n determined by GPC-MALLS-RI.

elevated temperatures (entries 4−6) can be used to favor this step, in the latter case leading to **7a** with molecular weights as high as 15.0 kDa (Figure S3).[20,21] ^{1}H and ^{31}P NMR analysis show that **7a** formed under the latter conditions has no detectable impurities beyond those assigned as end groups (aldehyde, carboxylic acid, and amide, Figure 2a),[22] while GPC analysis shows a monomodal size distribution with a polydispersity (ca. 2) typical of step-growth polymerizations. The reaction can be easily monitored by in situ ^{31}P NMR analysis. These show that the polymerization is remarkably efficient at each stage of the reaction and with no evidence for any defects (<1%) except for those representing end-groups (Figure 2b). This includes the final cycloaddition step to eliminate phosphine oxide, which is quantitative within NMR error. Interestingly, this end-group analysis suggests that this polymer is generated in higher molecular weights (M_n ∼ 67 kDa) than that shown by GPC analysis. Consistent with this, GPC-MALLS-RI analysis of this same polymer reveals its absolute molecular weight is closer to 51 kDa, or a degree of polymerization (DP) of 120 (Figure S4). The latter is the highest molecular weight of which we are aware for a multicomponent conjugated polymer synthesis.

A feature of this reaction is its ability to access conjugated polymers without presynthesized conjugated units: terephthaloyl chloride **5a** is a monomer used in large-scale polyamide production, and diimine **4a** is derived from terephthaldehyde and a primary amine, dimethylacetylene dicarboxylate (**6a**), a commercial alkyne, and (catechyl)PPh, which can be generated from catechol and dichlorophenylphosphine. As such, this conjugated polymer can be readily formed on multigram scale (Scheme 1). Systematic changes to the reaction conditions or stoichiometry can also be used to modulate the size and structure of **7a**. As an example, the use of a slight excess imine allows the generation of well-defined **7a′** with addressable aldehyde end groups (Scheme 1). Alternatively, dilution of the reaction, which inhibits the equilibrium formation of iminium salt, leads to lower molecular weight materials (Scheme S1). The polymerization can also be performed in a fully one-pot

*a. ^{1}H NMR Analysis of Polymer **7a***



b. In Situ ^{31}P NMR Analysis of Polymerization

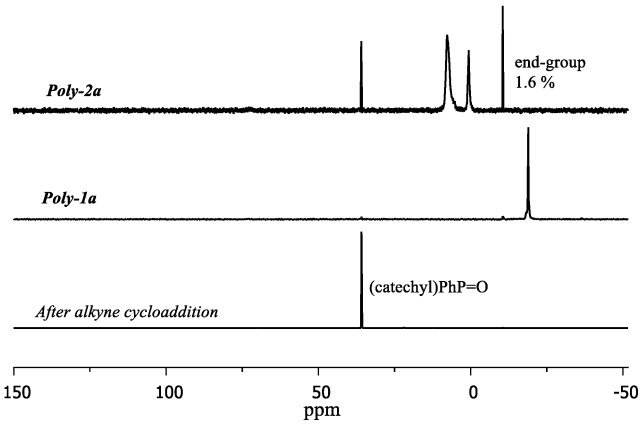
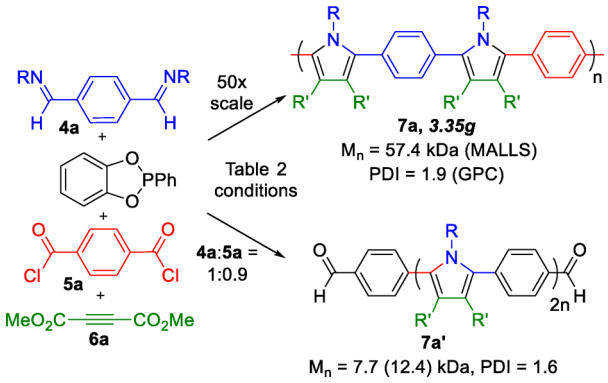


Figure 2. ^{1}H and ^{31}P NMR analysis of polymerization. (a) ^{1}H NMR spectra of **7a** with end groups in insets (a, aldehyde; b, carboxylic acid; c, amide end groups); (b) ^{31}P NMR analysis of each step in the polymerization.

Scheme 1. Systematic Control of Multicomponent Polymerization



fashion by using a stoichiometric amount of base with only a slightly lower molecular weight (M_n = 10.5 kDa, Scheme S2).

Polymer Diversity. Since this polymerization uses imine, acid chloride, and alkyne monomers, it is amenable to diversification. As shown in Figure 3, a range of diimines can be incorporated into this reaction. This includes carbazole (**4e**), fluorene (**4c**), and biphenyl (**4d**) imines, which form polymers with molecular weights as high as 40 kDa.[23] Heterocycles can also be added into the polymer backbone, such as thiophene and bis-thiophene (**4g,h**), while cross-conjugated polymers can

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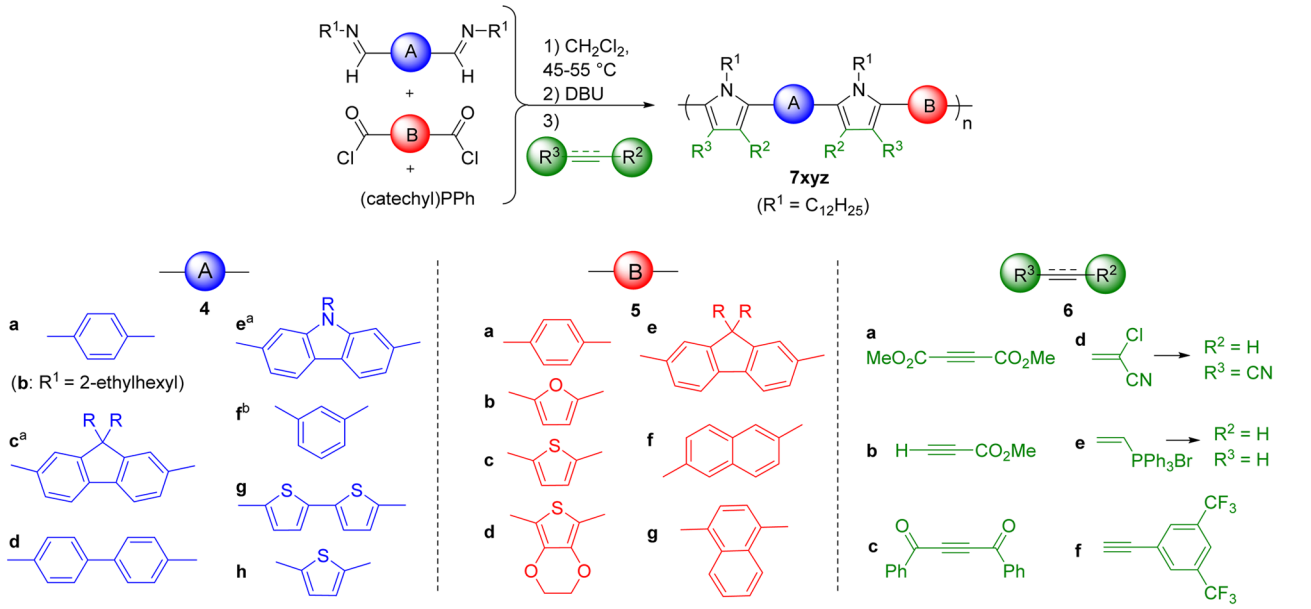

Monomer Combinations Employed[c]

Pdt	%[d]	M_n	PDI	DP	Pdt	%[d]	M_n	PDI	DP	Pdt	%[d]	M_n	PDI	DP	Pdt	%[d]	M_n	PDI	DP
7baa	63	11.3	2.1	31	**7gaa**	79	10.7	2.7	23	**7cea**	86	34.6	1.7	41	**7cac**	81	21.3	2.1	34
7caa	91	25.3	2.3	43	**7haa**	77	19.9	2.3	46	**7cfa**	76	40.7	1.9	67	**7cad**	74	15.1	2.1	31
7daa	98	24.4	2.3	43	**7cba**	84	22.3	2.0	39	**7cga**	87	30.1	1.7	57	**7cae**	69	24.7	1.8	56
7eaa	66	16.3	1.7	32	**7cca**	84	31.4	2.0	54	**7cab**	82	18.7	2.3	36	**7caf**	81	15.8	1.9	23
7faa	54	14.2	2.3	33	**7cda**	74	15.1	1.8	25										

Figure 3. Synthesis of conjugated polymer libraries from imine, acid chloride, alkyne, and alkene monomers. (a) R = 2-ethylhexyl. (b) R^1 = hexyl. (c) Polymers **7xyz** obtained from a combination of imine **4x**, acid chloride **5y**, and alkyne/alkene **6z**. Procedure of Table 2, entry 5. 0.10 mmol imine/acid chloride at 45−55 °C. See the Supporting Information for details. (d) Isolated yield of the reaction (%) after precipitation in methanol,[21] molecular weight M_n (kDa), and polydispersity PDI as determined by GPC in THF using polystyrene standards and the degree of polymerization DP are listed.

be generated with meta-substituted diimines (**4f**). Many of these monomers are formed from commercial and inexpensive dialdehydes. The acid chloride residue can be similarly modulated to incorporate other aromatic and heteroaromatic units, such as thiophene diacid chloride (available in one step from adipic acid) (**5c**), furans (accessible from 2,5-furan dicarboxylic acid, a breakdown product of cellulose) (**5b**), as well as various aromatic diacids (**5d−g**). Changes to the dipolarophile can be used to tune the pyrrole substituents (**6a−f**). Good regioselectivities were obtained for the unsymmetrical alkynes or alkenes examined (**6b,d,f**), which can be problematic for other variants of 1,3-dipolar cycloadditions to form pyrroles.[18c,24] This allows the one-pot synthesis of complex, regioregular conjugated polymers. Alternatively, electron-poor alkenes with halide or PPh_3 leaving groups can be cycloaddition partners (**6d,e**). These latter undergo aromatization upon HX loss to generate alternatively substituted products. Of note, vinylphosphonium bromide **6e** can be used as an acetylene equivalent to access unsubstituted pyrroles. Taken together, the diversity of the three monomers can allow the potential synthesis of over 300 structurally distinct conjugated polymers. We know of no other approach to conjugated polymers that provide such straightforward access to structural diversity, especially with high molecular weight control. As detailed in the Supporting Information (Table S1), analysis of the properties of these polymers shows that UV/vis absorbance and fluorescence can be modulated by over 100 nm within the polymers generated, and pyrrole fluorescent materials can be formed with quantum efficiencies of up to 76% for polymer **7cfd**, obtained from a **4c**, **5f**, **6d** combination of monomers.

Pyrrole-based polymers and copolymers have attracted attention for use as transistors, electrochromic devices, capacitors, electromagnetic shielding, and different types of sensors, although these materials are more classically generated from presynthesized pyrrole-containing monomers.[25] As such, we believe our multicomponent approach to pyrrole-containing polymers will provide a useful method to access new variants of these polymers, yet do so from combinations of substrates. As an example, from these 18 polymers, we selected **7caf** for testing in organic light-emitting diodes (OLED) based on its PL efficiency together with reasonable stability toward oxidation (as tested by cyclic voltammetry). Due to the rather low-lying HOMO level of this polymer (−5.56 eV vs vacuum level, obtained from CV), the use of cross-linkable hole-transport layers (xHTL) appeared mandatory.[26] The OLED had the layer stack ITO/PEDOT:PSS/QUPD/OTPD/**7caf**/TPBI/CsF:Al.[27] The EL emission occurs at 445 nm, in agreement with the PL wavelength, and the EL efficiency amounts to ca. 0.2 Cd/A, which is the highest reported for a pyrrole-containing polymer, although less than state of the art singlet-blue-emissive polymers.

We have preliminarily probed the ability of this platform to be employed in more targeted synthesis. Thiophene−pyrrole copolymers have been examined as materials for organic field

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effect transistors (OFET).[28] Previous syntheses of these polymers have involved electropolymerization[29] or multistep organic synthesis,[28,30] and formed insoluble or oligomeric materials. In contrast, the combination of the thiophene diimine **4h**, 2,5-thiophenedicarbonyl dichloride **5c** and (catechyl)PPh followed by vinyl phosphonium salt **6e** can allow the straightforward synthesis of the soluble, alternating thiophene-pyrrole copolymer **7hce** in good molecular weight (11.0 kDa, Figure 4a), and no evidence of structural defects.

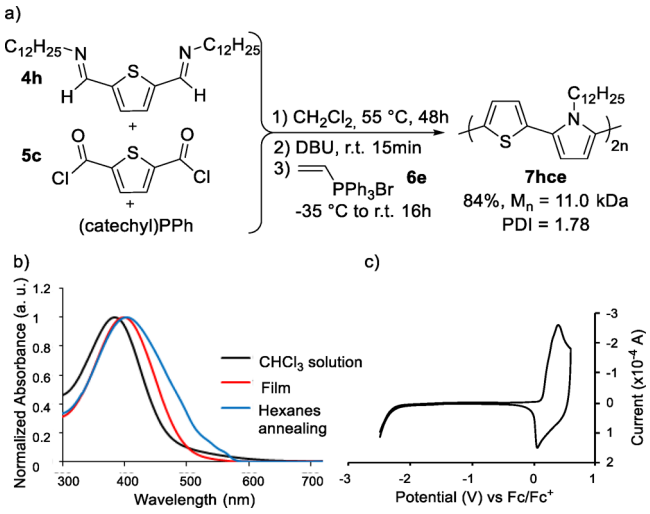

Figure 4. Multicomponent synthesis of thiophene/pyrrole copolymer. (a) Synthesis of **7hce**. (b) UV/vis in chloroform solution (black line) as thin film spincast from chloroform (red line) and thin film annealed in hexane vapor (cyan line). (c) Cyclic voltammogram (first cycle shown) of thin film in NBu_4PF_6/CH_3CN at 0.1 $V.s^{-1}$.

UV/vis analysis of this new polymer indicates novel spectral features that appear upon solvent annealing at longer wavelength (Figure 4b). In analogy to similar discussions on poly(3-hexylthiophene (P3HT),[31] we presume that the film is initially deposited in an amorphous state (as commonly observed for spin-casting) and that upon vapor annealing partial crystallization or aggregate formation of the polymer takes place in the solid state. This claim is further supported by OFET measurements, yielding a doubling of the charge carrier mobility upon solvent annealing (see the Supporting Information, Figure S5), indicative of the formation of a new phase with higher mobility, again in analogy with P3HT. Interestingly, electrochemical analysis shows that **7hce** can be more easily oxidized (starting at ca. 0.12 V, Figure 4c) than either of its two-component homopolymers, i.e., poly(*N*-alkylpyrrole) (ca. 1.0 V for the hexyl derivative; ca. 0.75 V for the methyl derivative)[32] and polythiophene (ca. 1.2 V).[33] Instead, the copolymer **7hce** features an oxidation onset approaching that of polypyrrole (ca. 0.1 V).[34] We attribute this to the structure of **7hce**, where the alternating pyrrole/thiophene polymer accessible via this multicomponent approach leads to strongly reduced steric hindrance in the solid state and creates a soluble, electron-rich polymer similar to that of polypyrrole.

■ CONCLUSIONS

In conclusion, we have developed a new multicomponent synthesis of conjugated polymers. This approach allows the synthesis of high molecular weight, pyrrole-containing polymers directly from combinations of diimines, diacid chlorides, and alkynes/alkenes. The wide monomer scope of this reaction can provide a route to form families of conjugated polymers where in one step every unit in the polymer can be independently modified. Experiments directed toward exploiting this multicomponent approach to access new classes of functional polymers are currently underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b05035.

Experimental procedures and characterization data for all products (PDF)

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Notes

The authors declare no competing financial interest.

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