Oligomer Synthesis

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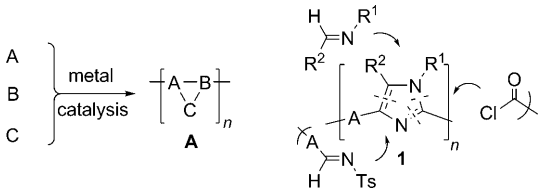
A Palladium-Catalyzed Multicomponent Coupling Approach to π-Conjugated Oligomers: Assembling Imidazole-Based Materials from Imines and Acyl Chlorides**

*Ali R. Siamaki, Marc Sakalauskas, and Bruce A. Arndtsen**

π-Conjugated poly-heterocycles, as well as soluble and more-processable oligo-heterocycles, have been the subject of significant research efforts over the past several decades.[1,2] These materials display an array of interesting fluorescence, electro-optical, and electronic properties, and have found application as components in semiconductors,[3] photovoltaic cells (PVC),[4] field-effect transistors (FET),[5] optical devices (e.g., OLEDs),[6,7] and sensors.[8] A useful property of conjugated materials is their tunability, wherein changes to their structure, including the backbone aromatic units, ring connectivity, and substituents, can dramatically influence the conjugated length, the HOMO–LUMO band gap, and chain–chain interactions.[9] This has stimulated significant efforts towards preparing new variants of these materials. In this regard, the construction of oligo- or poly-heterocycles typically involves either electropolymerization,[9,10] or, more commonly, the metal-mediated coupling of halogenated and metalated heterocycles.[11] While both methods are very effective, one feature they share is the need to initially prepare the heterocyclic units prior to polymerization. In the case of more complex, tuned structures, the synthesis of the monomer unit itself can require a challenging multistep synthesis. The latter can make it more difficult to access these materials, as well as modulate the product structure, since it requires the synthesis of each new monomer unit.

In principle, an attractive alternative approach to conjugated materials would be to consider their structure to be made up of multiple simple monomers assembled together at once, rather than from preformed heterocycles. The challenge is how to assemble a structure as complex as a conjugated, substituted oligo-heterocycle from available substrates. In this regard, transition-metal catalysis can be a useful tool because of its ability to activate typically unreactive monomers towards polymerization. This has been extensively employed in the synthesis of polymers from simple monomers.[12] However, another possibility would be to use the reactivity of metal catalysts to control the assembly of multiple differing versions of available units to form new and more elaborate structures (Scheme 1).



Scheme 1. A multicomponent approach to oligoimidazoles. Ts = 4-toluenesulfonyl.

Although multicomponent reactions have become of relevance in small-molecule synthesis and library development,[13] they are significantly underexplored in the realm of macromolecule synthesis, a field for which they are arguably at least as relevant. The examples by Endo, Tomita, and co-workers, and Yokozawa and co-workers have involved the efficient construction of co-polymers of multiple monomers.[14] As an alternative, we show herein how metal catalysis can allow the assembly of multiple simple units into a completely new and well-defined conjugated repeat unit (**A**; Scheme 1), in the form of oligoimidazoles **1**. To our knowledge, this general approach has not been previously demonstrated, and provides access to conjugated materials **1** in one-pot reactions from monomers that are each accessible and easily diversified. The latter creates a platform to readily form and tune these structures.

Our approach to this synthesis considers imidazole-based conjugated materials **1** to arise from imines, diimines, and di(acyl chloride)s, rather than as a series of linked, preformed imidazoles. Palladium catalysis can provide a potential mechanism to selectively couple these units together by mediating the series of steps outlined in Scheme 2. This approach is based on our recent efforts in metal-catalyzed multicomponent reactions,[15] including imidazole synthesis,[16] and involves the catalytic synthesis of mesoionic 1,3-oxazolium-5-oxides, commonly referred to as Münchnones (**2**), from imines, acyl chlorides, and CO (steps a–e).[15a] By coupling this synthesis with the ability of **2** to undergo 1,3-dipolar cycloaddition with imines, and subsequent aromatization (step f), an overall route to selectively synthesize **1** from the three monomers in a single catalytic operation would result.

The substrates examined in this reaction were: commercial terephthaloyl chloride **3** (a component in polyamide synthesis), imine **4**, and **5**, which was generated from

[*] A. R. Siamaki, M. Sakalauskas, Prof. B. A. Arndtsen
Department of Chemistry, McGill University
801 Sherbrooke St. W. Montreal, H3A 2K6 Quebec (Canada)
Fax: (+1) 514-398-3797
E-mail: bruce.arndtsen@mcgill.ca

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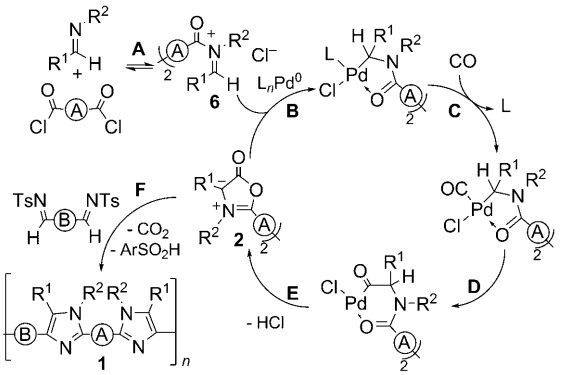
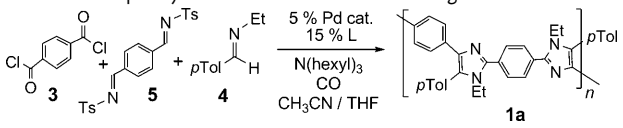


Scheme 2. Potential mechanism for the multicomponent cascade.

terephthaldehyde and sulfonamide.[17] As shown in Table 1, the coupling of these units in the presence of [Pd_2dba_3] catalyst does indeed result in the formation of **1a**, albeit in

Table 1: A one-pot synthesis of imidazole-based oligomers.[a]



Entry	Pd	Ligand	Additive	Yield [%][b]
1	[Pd_2dba_3]	Bu_4NBr	–	25
2	**8**	PPh_3	–	–
3	**8**	P(*o*-Tol)$_3$	–	48
4	**8**	P(*o*-Tol)$_3$	LiCl	51
5[c]	**8**	P(*t*Bu$_2$)2-biphenyl	–	70
6[c,d]	**8**	P(*o*-Tol)$_3$	–	72
7[c,e]	**8**	P(*o*-Tol)$_3$	–	68

[a] **3** (50 mg, 0.25 mmol), **5** (118 mg, 0.25 mmol), **4** (72 mg, 0.49 mmol), *N*(hexyl)$_3$ (199 mg, 0.74 mmol) 45 °C, 16 h; [{Pd(C(H)TolNEtCOPh)Cl}$_2$] (**8**); 4 atm CO. [b] Yield of isolated product. [c] **5** after 16 h. [d] $M_w = 3.1 \times 10^3$, PDI = 1.16. [e] 0.5 % **8**; all other reagents at 10× scale of [a].

very low yield (25 %). Examination of the reaction mixture shows a major product of the reaction is the iminium salt intermediate **6**, which implies that the oxidative addition of this substrate to palladium (step b) may be slow. This can in principle be favored by forming a more-electron-rich palladium catalyst. Replacing dba with a stronger donor, PPh_3, inhibits the reaction (entry 2), presumably because of its strong coordination to palladium blocking subsequent carbonylation (step c);[15] however, bulky, electron-rich phosphines can increase yields to 48 % (entry 3). A second byproduct in this reaction is the α-sulfonyl-substituted amide **7**,[18] which results from the reaction of $TolSO_2^-$ with the in situ generated **6**. While our previous approaches have shown that the formation of **7** can be suppressed by LiCl,[16] the latter has little influence on this transformation. However, by first generating **2**[19] and then adding component **5**, the formation of **7** is inhibited, allowing the generation of **1a** and its isolation in good yield using a catalyst loading as low as 0.5 mol % palladium (entry 7).

The reaction shown in Table 1 provides an efficient, alternative approach to assemble a conjugated oligo-heterocycle from three available monomers. **1a** is formed with regioregularity, as anticipated from the mechanism, and in moderate molecular weights (3 to 6 kDa as determined by GPC analysis, Table 2). **1a** is of sufficient length to display fluorescent properties (see below). The structure of **1a** was additionally confirmed by MALDI/TOF-MS and ESI-MS analysis, which shows the presence of the imidazole/phenylene/imidazole repeat units. End-group analysis reveals **1a** is terminated with imine and a carboxylic acid functional groups. The latter presumably results from the sulfinate anion (p-$TolSO_2^-$) liberated upon condensation of **2** and **5** (Scheme 2) undergoing reaction with the Münchnone unit, and subsequent disproportionation,[20] thus leading to the termination step of the chain growth.

Imidazole-containing materials have attracted interest as potentially reactive, electron-acceptor units within conjugated polymers, and display intense blue emission brought on by π conjugation.[21] The products **1** generated in this multicomponent synthesis show similar properties. **1a** has a moderate energy absorbance at $\lambda_{abs} = 320$ nm (CH_2Cl_2), and a strong blue emission ($\lambda_{em} = 469$ nm). However, in addition to simply forming **1a**, this approach is also amenable to diversification, wherein any of the three building blocks can be systematically varied. This variation provides a tool to effectively modulate conjugation. For example, a series of imines can be incorporated into the reaction from available aldehydes and amines (Table 2). This includes the use of the longer alkyl-chain-substituted imine **1b**, as well as those

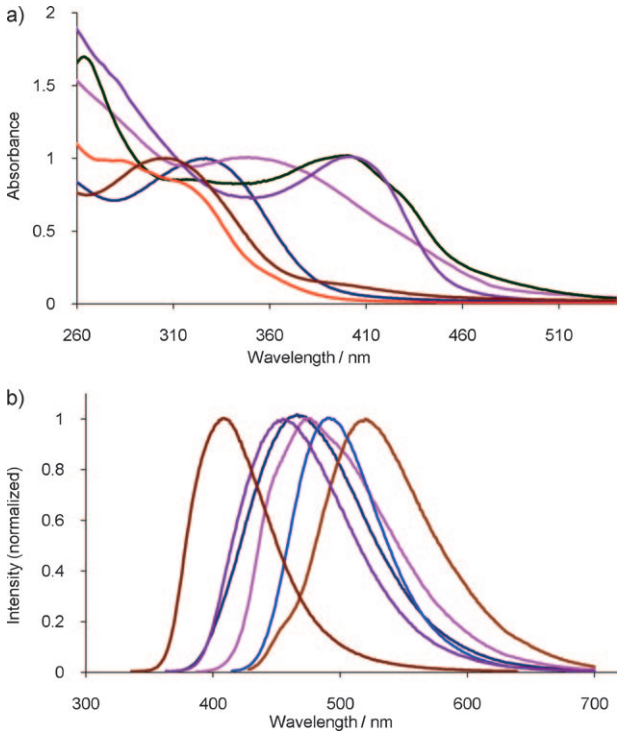


Figure 1. a) UV/Vis absorption and b) fluorescence emission spectra of products **1** (CH_2Cl_2 solution). **1b**: blue; **1d**: pink; **1e**: purple; **1f**: green; **1g**: orange; **1i**: brown.

Table 2: Diversity of materials through multicomponent assembly.[a]

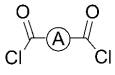
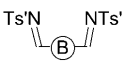
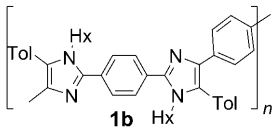
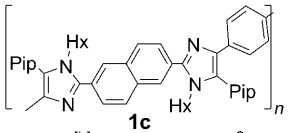
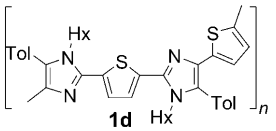
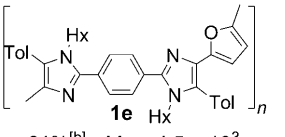
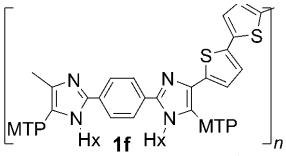
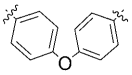
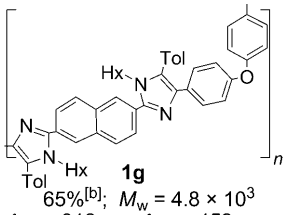
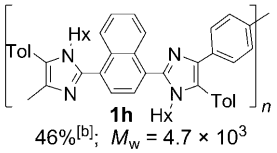
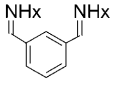
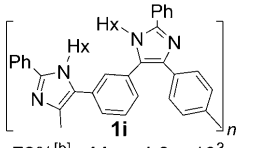
			Product
			 **1b** 70%[b]; $M_w = 5.4 \times 10^3$ $\lambda_{abs} = 320$ nm, $\lambda_{em} = 470$ nm
			 **1c** 68%[b]; $M_w = 5.2 \times 10^3$ $\lambda_{abs} = 330$ nm, $\lambda_{em} = 478$ nm
			 **1d** 54%[b]; $M_w = 5.5 \times 10^3$ $\lambda_{abs} = 351$ nm, $\lambda_{em} = 481$ nm
			 **1e** 61%[b]; $M_w = 4.5 \times 10^3$ $\lambda_{abs} = 403$ nm, $\lambda_{em} = 497$ nm
			 **1f** 74%[b]; $M_w = 4.4 \times 10^3$ $\lambda_{abs} = 401$ nm, $\lambda_{em} = 529$ nm
			 **1g** 65%[b]; $M_w = 4.8 \times 10^3$ $\lambda_{abs} = 312$ nm, $\lambda_{em} = 459$ nm
			 **1h** 46%[b]; $M_w = 4.7 \times 10^3$ $\lambda_{abs} = 326$ nm, $\lambda_{em} = 460$ nm
			 **1i** 72%[b]; $M_w = 4.8 \times 10^3$ $\lambda_{abs} = 300$ nm, $\lambda_{em} = 415$ nm

Table 2: (Continued)

			Product
			1j 64%[b]; $M_w = 4.5 \times 10^3$ $\lambda_{abs} = 302$ nm, $\lambda_{em} = 413$ nm

[a] Reaction conditions as for entry 6 of Table 1. [b] Yield of isolated product. Hx = hexyl.

derived from electron-donor or electron-acceptor aromatic aldehydes. Even more dramatic changes to the conjugated backbone can be made through modifying the diimine or di(acyl chloride) building blocks, such as the use of heterocyclic units in the imine or acyl chloride fragments **1d**, or even using different combinations within a single oligomer **1e**–**1h**. In addition to the linking groups, the actual core connectivity can also be modified. Thus, a combination of two different diimines with benzoyl chloride leads to the generation of 4,5-substituted **1i** and **1j**, where conjugation occurs through the adjacent carbon atom on the imidazole ring. Together, this can provide access to a range of backbone-conjugated materials (e.g., imidazole/thiophene, imidazole/furan), or multiple combinations of units within a single product (e.g., phenylene/imidazole/thiophene).

As anticipated, these structural modifications directly influence conjugation. For example, disruption of backbone conjugation (**1g**, **1i**, **1j**) leads to an increase in absorbance energy (**1g**: $\lambda_{abs} = 312$ nm, Figure 1). A similar trend is observed with the fluorescence. Alternatively, the introduction of other heterocyclic units into the structure, such as thiophene or furan (**1d**–**f**), results in a red-shift in the absorbance and fluorescence emission (by up to 100 nm; **1f**: $\lambda_{abs} = 401$ nm; $\lambda_{em} = 529$ nm). Such donor–acceptor (thiophene–imidazole) conjugated materials have recently attracted significant attention because of their ability to modulate their band gap, HOMO–LUMO energy, and increase exciton lifetime for use in photovoltaics.[22] The blue-green emitting **1d**–**f** compare favorably to these materials,[23] as well as ladder-type (*p*-phenylene)s (LPPPs),[24] yet are synthetically accessible, soluble, and can be easily modulated by changes to the spacer and substituents.

From a product discovery standpoint, this amenability to structural diversity in Table 2 can be an important research tool. For example, polymer libraries have attracted increasing attention as an intriguing tool to rapidly optimize and modulate structures.[25] However, many macromolecule syntheses are not well suited for core structural diversification, and often have only one or two easily varied monomers to achieve structural diversity. In contrast, the three-component nature of this reaction makes it straightforward to generate families of structurally distinct oligomers. As a preliminary illustration of this feature, a pool of three imines, four diacids,

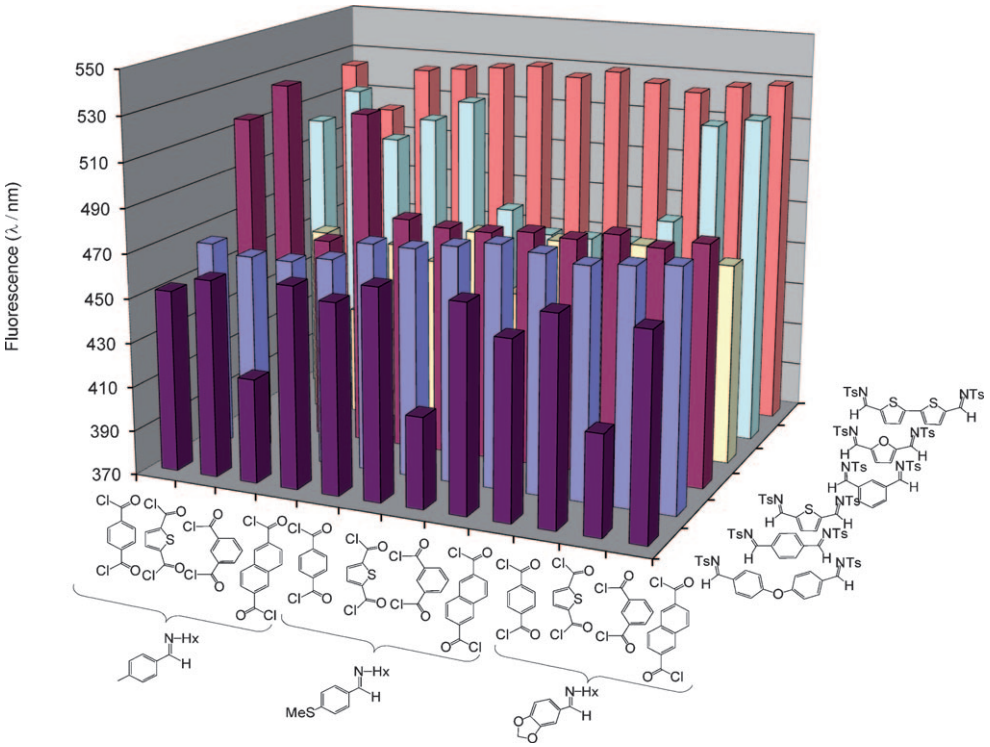


Figure 2. Fluorescence emission maxima (nm) of a library of 72 conjugated imidazole-containing materials.

and six diimines has been used to generate a macromolecule library of 72 different conjugated imidazole-containing materials, each formed by the one-step, palladium-catalyzed reaction (Figure 2).[26] This example represents a unique example of a macromolecule library where any unit either within or about the π-conjugated core can be selectively modified at the same time that the core is assembled. The approach provides access to materials incorporating various combinations of aromatic linkers, co-oligomers of several heterocycles, or backbone substituents. While the properties of these materials are still under investigation, as shown in Figure 2, such structural changes can allow fluorescent emission to be systematically tuned by over 130 nm from a high band gap to blue- or green-emitting materials, depending upon the monomer combinations employed. The latter fine-structural control provides an approach to selectively modulate band gap and HOMO–LUMO energies, both of which are important in the design of extended π-conjugated systems with targeted properties, and do so without having to individually assemble each heterocyclic unit.

In conclusion, these results illustrate a new approach to synthesize oligomeric materials: by the simultaneous assembly of multiple simple monomers into a new and well-defined repeat unit (Scheme 1). A feature of this approach is the availability of building blocks, which includes di(acyl chloride)s such as terephthaloyl chloride **3**, dialdehydes such as terephthaldehyde in **5**, simple amines, and aldehydes. By assembling multiple versions of these monomers together at once, this provides an alternative route to construct macromolecules in a straightforward and diversifiable fashion. Studies towards the use of this multicomponent coupling approach to prepare alternative classes of materials, as well as further investigations of the properties of **1**, such as its coordination and cation sensing properties, are currently in progress.

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