# Final Technical Report

From a materials property perspective, $sp^2$ hybridized carbon and predominantly-carbon structures have demonstrated some of the most novel physical properties including ferromagnetism,[1-3] metallic conductivity and superconductivity (in graphite intercalation compounds),[4] negative Poisson ratios[5,6] and high lithium ion storage capacities.[7,8]  The dominant problem preventing the use of fused aromatic polymers is that they are not processable. They are, in virtually every case, insoluble and cannot be melted.  The only viable approach that has emerged for exploiting these materials is fabrication and/or patterning via a precursor polymer.  The most attractive precursor would be convertible from an insulator to a metallic conductor directly under the application of some form of patterning radiation.  Any process in which a material is directly transformed into patterns with the desired features (termed "direct writing", Figure 1) is much more efficient than one in which a photoresist must be employed. This is because photoresist is ultimately sacrificed and acts only as a template − additional steps are required to install the material of interest.



**Figure 1.  Schematic depiction of direct writing.  Conversion of an insulating material directly into a conducting material upon application of light would require no metallization, strip or lift-off steps.**

Virtually all examples of direct writing involve the selective deposition of metal features. For example, laser assisted direct writing of copper on poly(imide) produces micron-sized lines with good conductivity and adhesion to the substrate.[9,10]  As one miniaturizes conducting features to the nanometer scale, metals become unattractive as they fail due to electromigration under the application of an electrical bias.[11-13]  Conjugated/aromatic polymers should not be able to electromigrate as this would require breaking covalent bonds or migration of entire polymer chains in the matrix – both unlikely processes.  ***It remains untested as to whether these types of materials can be highly conducting and capable of being patterned at the nanometer scale.***

Direct writing of conducting, carbon-based materials has been proposed but, as described below, is not well developed.  Direct writing at the nanometer scale requires a route that produces a highly conducting material since features of this size have large resistances even when the materials composed of them are highly conductive.  There have been several intriguing demonstrations of direct writing on conjugated polymers and their precursors.  These studies have demonstrated such things as the production of nanometer scale patterns via near-field

optical microscopy writing,[14] photopatterning of diacetylenes,[15] patterned luminescent polymers,[16, 17] creation of micro electromechanical (MEMS) structures of glassy carbon,[18, 19] and fabrication of electrochemically modulated optical diffraction gratings.[20] These reports did not focus on achieving high contrast in the relative electrical conductivity between exposed and unexposed material, however. Photoinduced doping and photolithographic patterning of poly(methyl aniline) produced patterns with a conductivity of $10^{-3}$ S/cm, but only after HCl exposure.[21] Poly(thiophene) derivatives have been patterned photolithographically but require subsequent wet-etching to define the pattern of the polymer.[22-24] Poly(butadiene) films have been simultaneously isomerized and iodine doped to form conducting patterns with a conductivity of ca. $10^{-5}$ S/cm.[25] Selective laser irradiation of BBL produced conducting lines of this material at relatively large length scales.[26] Such demonstrations, while illustrative, do not meet the criteria set for a successful direct writing of polymer-based electrical connects or circuitry, particularly if it is desired to write at the nanometer scale.

Several routes to synthesize graphitic material or aromatic ladders[27-29] exist. However, none appear adequate for the conversion of the material to a conductive form that satisfies the following criteria. *Each of these issues would defeat attempts to form micrometer-scale to nanometer-scale patterns of conducting material by direct writing (Figure 1).*

●  The precursor polymer is straightforward to synthesize – minimal chemical synthesis of the monomer units is required.

●  The precursor polymer can form durable films so that it is applicable to the preparation of devices and carbon circuitry. In some cases, the precursor is not very soluble and requires strong acids to process it. In other cases, the precursor does not form mechanically stable films.

●  The synthetic route is amenable to the installation of chemical functionalities so that binding/transduction elements can be introduced for sensor applications and the photophysical and electronic properties of these polymers can be tuned.

●  The final polymer displays high electrical conductivity.

●  The conversion of the precursor takes place under mild heating or photochemical conversion – e.g. no chemical reagents are required that cannot operate in the solid state. This criterion is typically the one that current materials are least able to meet. Often, the conversion of the precursor polymer requires high temperatures. When chemical reagents are employed in the conversion, they are typically harsh and likely produce additional, degradative reactions on the polymer chain.

●  It is possible to characterize the final polymer reasonably well.

Our approach to new precursor polymers for direct writing is shown in Scheme I below. This route involves cyclization of benzylic nitriles – as we show below on model oligomers, aromatization takes place via tautomerization. This route meets all of the criteria for direct writing elucidated above.

**Scheme I. Proposed Route to an aromatic ladder polymer amenable to photolithographic patterning.**
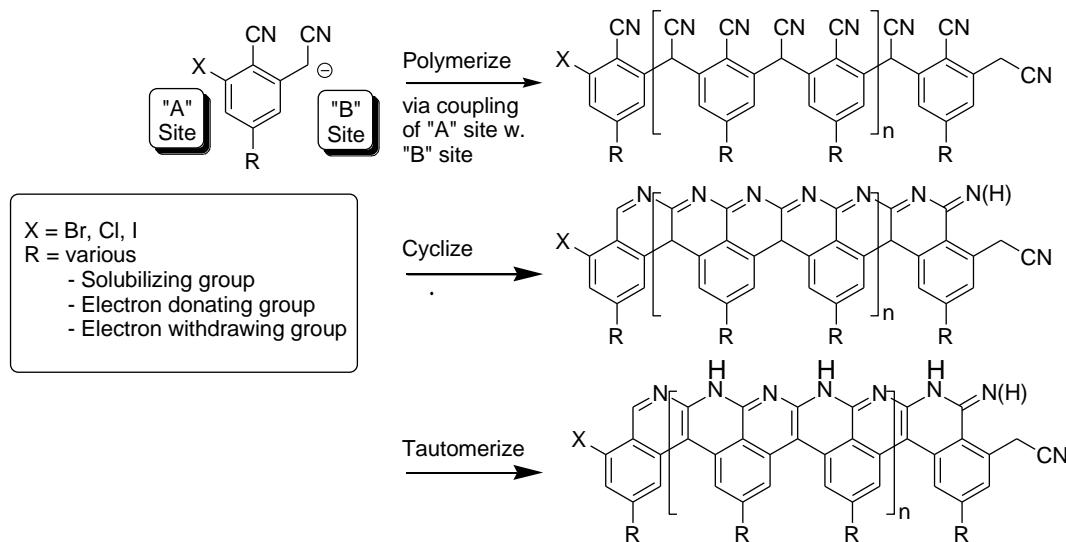


We have published four contributions as the result of the work in this grant:

1. "Cascade cyclization to produce a series of fused, aromatic molecules" Behof, W. J.; Wang, D.; Niu, W.; Gorman, C. B. *Org. Lett.*, **2010**, *12 (9)*, 2146–2148 (Selected as SynFact of the month: *Synfacts* **2010**, *7*, 0763-0763)
2. "Aminoisoquinolines as Colorimetric Hg$^{2+}$ Sensors: The Importance of Molecular Structure and Sacrificial Base" Wan, Y.; Niu, W.; Behof, W. J.; Wang, Y.; Boyle, P., Gorman, C. B. *Tetrahedron*, **2009,** *65*, 4293-4297.
3. "Efficient synthesis of halo indanones via chlorosulfonic acid mediated Friedel-Craft cyclization of aryl propionic acids and their use in alkylation reactions" Sharma, A. K.; Subramani, A. V.; Gorman, C. B. *Tetrahedron* **2007**, *63*, 389–395.
4. "Chlorosulfonic Acid" Sharma, A. K.; Gorman, C. B. in *e-EROS Encyclopedia of Reagents for Organic Synthesis,* Paquette, L. A.; Crich, D.; Fuchs, P. L.; Molander, G. eds.; John Wiley & Sons, Ltd. DOI: 10.1002/047084289X.rc148.

# 1 Synthesis of the precursor polymer

## 1.1 An efficient route to the monomer

The desired monomer couples an aryl halide to a benzyilic anion (functionalities "A" and "B", respectively, Scheme I) Our first synthesis of the monomer was performed in six steps as shown in Scheme II. Even though it was a long synthesis, it was successful where other, simpler approaches failed.

**Scheme II. Original A-B monomer synthesis.**
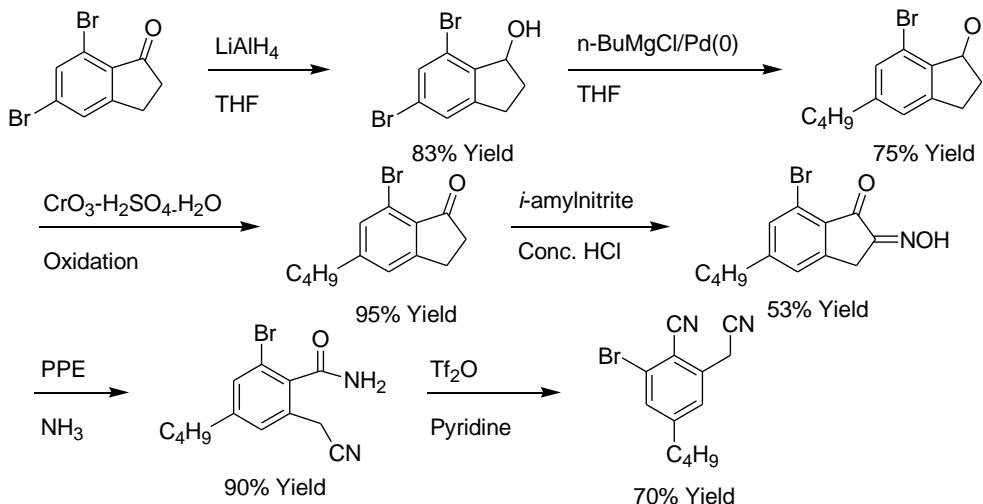


A simpler route to the monomer was highly desirable, however. We successfully designed and implemented the route illustrated in Scheme III. It requires only four steps, each of which involve simpler purification protocols and are more amenable to scale-up compared to the steps shown in Scheme II. The Sandmeyer reaction (step 2) is modest in yield but can be performed on a large scale and with several, commercially available and inexpensive *para*-substituted aniline derivatives. Thus, variation of the functionality in the *para* position is very straightforward. The final two steps occur in excellent yields with straightforward purification. Moreover, both can be conducted under microwave irradiation in very short times. We now have gram quantities of several monomer derivatives in hand and can focus exclusively on making polymers.

**Scheme III. Improved synthetic route to A-B type monomer.**
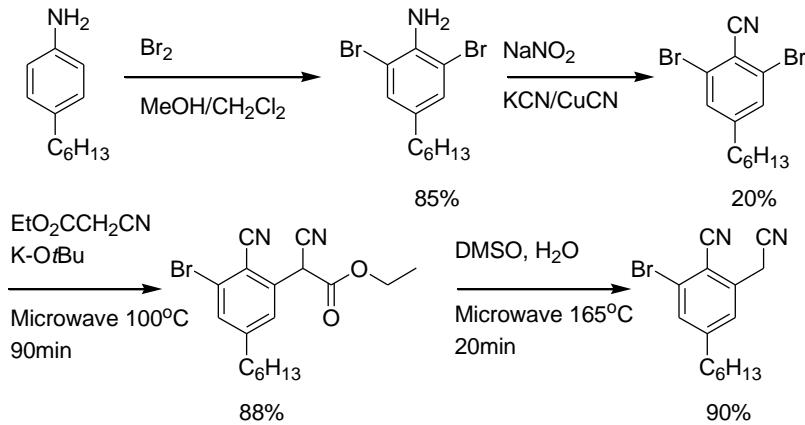
## 1.2 Precursor polymer synthesis via palladium-catalyzed coupling of an A-B type monomer

### 1.2.1 Synthesize polymer

We have explored palladium-catalyzed polymerizations of this monomer under a variety of conditions. Table 1 shows some selected examples.  It shows that the proposed coupling reaction works.  However, from the variability in yield and molecular weight with differing conditions, we conclude that the choice of base and phosphine in this reaction are important. Thus, we have made polymer, but molecular weights are low, and these conditions need to be optimized.  In optimization, it is helpful to have several options.  To this end, we are currently working on three routes to increase the molecular weight of the polymer.  These are presented in turn in Sections 1.2.2 through 1.2.4 below.  This work does not preclude our study of these polymers as materials and in potential applications.  To this end, we are using these polymers in deposition and electrospinning experiments described later in this proposal.

**Table 1.  Polymerizations using A-B monomer with hexyl side chain.**
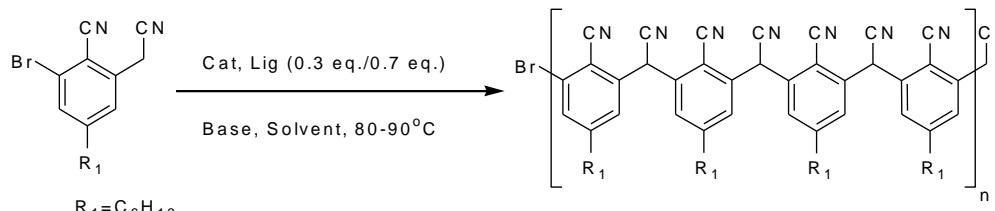


|   | Pd | L | Base | Solvent | Time (h) | % Yield | Mn (GPC) |
|---|---|---|---|---|---|---|---|
| 1 | Pd(OAc)$_2$ | P($t$Bu)$_3$ | Na-O$t$Bu | THF | 48 | 60 | 1900 |
| 2 | Pd$_2$dba$_3$ | Q-Phos | Na-O$t$Bu | THF | 48 | 0 | 0 |
| 3 | Pd(OAc)$_2$ | BINAP | Na-O$t$Bu | THF | 48 | 35 | 1600 |
| 4 | Pd(OAc)$_2$ | P($t$Bu)$_3$ | Na-O$t$Bu | THF | 24 | 43 | 1300 |
| 5 | Pd(OAc)$_2$ + 0.15 eq. CuI | P($t$Bu)$_3$ | Na-O$t$Bu | THF | 24 | 35 | 1400 |
| 6 | Pd(OAc)$_2$ | P($t$Bu)$_3$ | Na-O$t$Bu | DMF | 24 | 49 | 1200 |
| 7 | Pd(OAc)$_2$ | P($t$Bu)$_3$ | Na-OMe | THF | 24 | 36 | 1100 |
| 8 | Pd(OAc)$_2$ | P($t$Bu)$_3$ | Na$_2$CO$_3$ | THF | 24 | 0 | 0 |
| 9 | Pd(OAc)$_2$ | P($t$Bu)$_3$ | Li N(SiMe$_3$)$_2$ | THF | 24 | 0 | 0 |
| 10 | Pd(OAc)$_2$ | P($t$Bu)$_3$ | Li-O$t$Bu | THF | 24 | 66 | 1000 |

| | Pd | L | Base | Solvent | Time (h) | % Yield | Mn (GPC) |
|---|---|---|---|---|---|---|---|
| 11 | Pd(OAc)$_2$ | P($t$Bu)$_3$ | K-O$t$Bu | THF | 24 | 0 | 0 |

## *1.2.2    Optimize the palladium-catalyzed coupling conditions*

There is a growing body of literature in which the factors influencing the efficiency of palladium-catalyzed coupling reactions have been elucidated and optimized.  We propose that optimization of our polymerization can successfully follow these protocols.  For example, Hartwig showed that it was difficult to couple enolate anions with cyanophenyl halide but was possible when the cyano was substituted with a trifluoromethyl group (Scheme IV).[30]  Verkade, however, showed that use of his phosphine was successful in a similar reaction (Scheme V).  Further, in this work, it is stated that "…cyanoacetate esters did not couple with aryl bromides possessing electron withdrawing groups such as esters, ketones and nitriles in the presence of the Pd(Ph$_5$C$_5$)-Fe(C$_5$H$_4$)P($t$-Bu)$_2$ or Pd/P($t$-Bu)$_3$ catalyst systems".[31]  These observations illustrate the importance of the choice of supporting phosphine.

**Scheme IV**
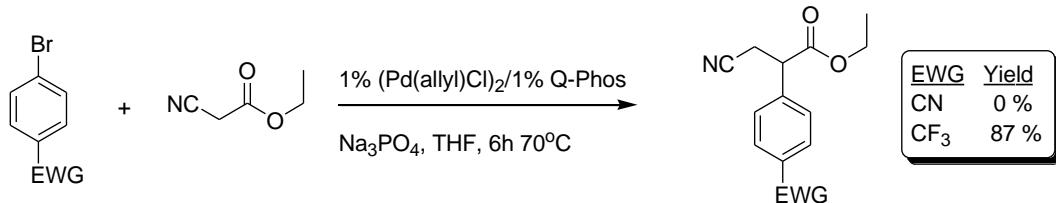


**Scheme V**
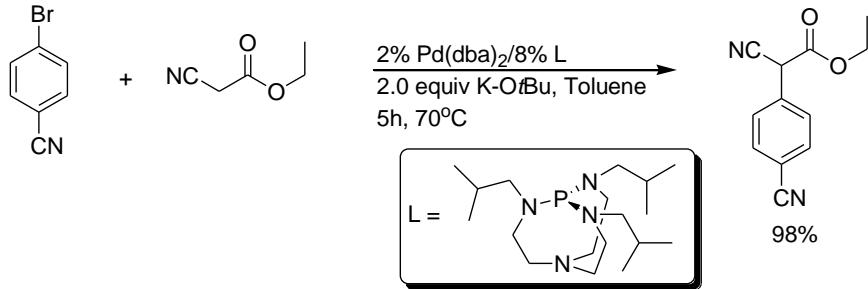


These observations lead us to the following proposed reactions.  These are being explored to maximize both yield and molecular weight.

1.    Examine more broadly the effect of phosphine on the polymerization.  This includes the examination of Verkade's phosphines and also the biphenyl-based phosphines pioneered by Buchwald et al.[32]
2.    Examine the polymerization under microwave conditions.  Note that in our microwave reactor, we can scale these reactions up to ca. 80 mL size, potentially producing quite a bit of polymer in one reaction
3.    Examine the effect of non-polar solvents.  In particular, we have found several examples in the literature of palladium-mediated coupling of an aryl halide with an enolate anion equivalent where toluene is the preferred solvent.

4.      Vary the amount and type of base.  Note that in both Scheme IV and Scheme V, the benzylic proton of the product is more acidic than the benzylic protons of the starting material.  Comparison of similar compounds shows a pKa difference of ca. 4-5.[33]  One might then ask why the product does not do proton transfer with the starting material?  This would limit the yield of the reaction to 50% if only 1 equivalent of base were used (in a number of literature reactions one equivalent of base was added). Our monomer likely has very acidic protons.  Although we have shown that bases as mild as sodium carbonate do not produce any polymer, there are a number of choices for base that are more basic than this yet much less basic than sodium *tert*-butoxide.

*1.2.3    Explore conditions for facile nucleophilic aromatic substitution*

**Scheme VI.  Proposed mechanistic scheme illustrating the competition between nucleophilic aromatic substitution and deprotonation.**
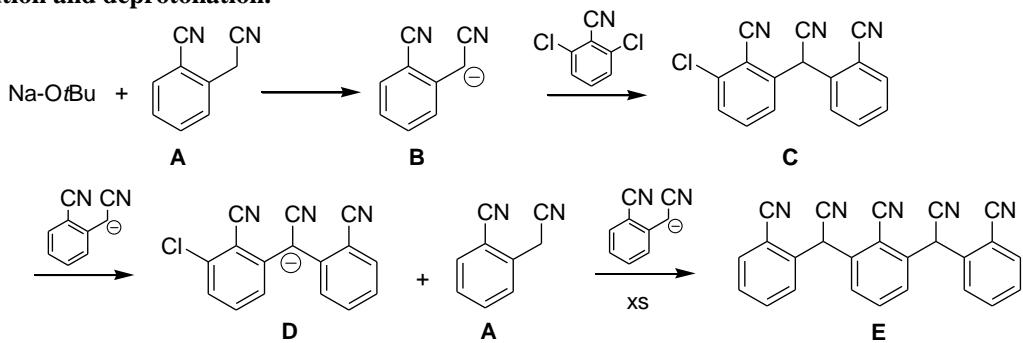


One might ask whether this chemistry could occur in the absence of palladium.  From the results above, there are issues in optimizing the chemistry.  Moreover, palladium is costly and is not always easy to remove from polymeric materials at the end of the synthesis.  Thus, a second option worth pursuing is coupling via nucleophilic aromatic substitution of the benzylic anion at the aryl halide position.  We have begun to investigate this option.  In $d_8$-THF, the reaction shown in Scheme VI was monitored by ^{1}H NMR.  The clean spectral signature of the benzylic anion (**B**, the result of step 1) disappeared upon addition of 2,6-dichloro benzonitrile.  However, instead of observing the methine proton of the product **C** (at ca. 6.1 ppm as confirmed by independently synthesizing the compound), a different anion was observed along with *o*-cyanobenzonitrile.  Proton transfer occurred to give the deprotonated dimer **D**.  Adding more base does facilitate formation of more of **B,** but, not surprisingly, nucleophilic aromatic substitution at the now electron rich **D** is not facile. Using excess of anion **B**, the desired trimer (**E**) could be obtained but only in 20% yield under these conditions

If we can avoid this proton transfer (e.g. as must have been avoided in a number of literature examples where only one equivalent of base was added), we might be able to omit the palladium catalyst.  Will a less polar solvent such as toluene ameliorate this problem?  We are examining this at present.  Nucleophilic aromatic substitution is more facile with aryl chlorides and fluorides.  We are preparing the chloro and fluoro derivatives of the monomer at present with solubilizing alkyl groups on the arene rings that will aid solubility in less polar solvents.

## 1.2.4    *Explore other A-B couplings using masked/softer anion equivalents*

Problems with proton transfer, sensitivity to the counterion, etc. are all hazards of using carbanions.  Can we use other functionalities that react with palladium as a carbanion would?  We think several options are worth exploration.

**Scheme VII.**

Completed Model Reaction
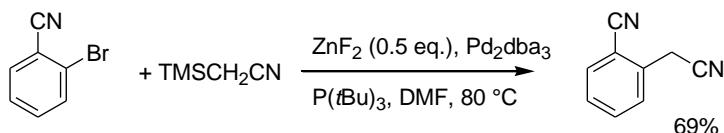


Proposed Reaction
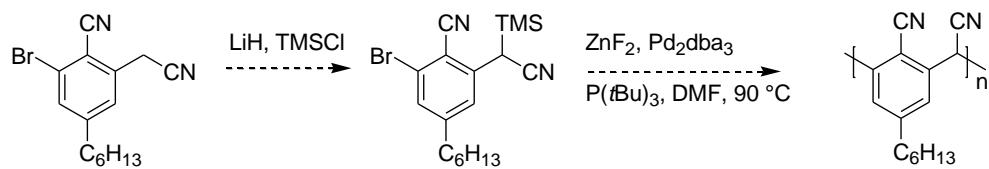


In Scheme VII, removal of TMS with zinc fluoride is employed *in lieu* of base.  Hartwig showed that trimethyl silyl acetonitrile can act as an acetonitrile anion equivalent in the presence of zinc fluoride.[34]  We showed that trimethylsilyl acetonitrile can couple with *o*-cyano bromobenzene under these conditions (Scheme VII, top).  We are now extending this to the A-B monomer (Scheme VII, bottom).  Hartwig's conditions are quoted for step two of this scheme.

**Scheme VIII.**
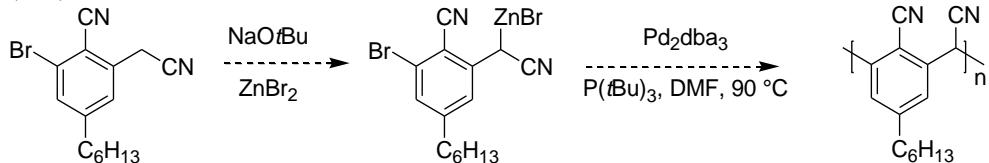


In Scheme VIII, use of an organozinc reagent is proposed, either generated *in situ* or isolated.  In this scheme, no base is required during polymerization.  Palladium transmetallates well from zinc. [35]  In Scheme XI, the strategy is to couple a phenyl boronic acid with a benzylic bromide.  Nobre et al. showed that p-cyano benzyl bromide can couple with phenyl boronic acid in the presence of $Pd(OAc)_2/PPh_3/K_3PO_4$/toluene in 99% yield.[36]  This chemistry can possibly be extended as shown.  Our proposed synthesis of the A-B type monomer is shown in the first four steps of Scheme IX.  Trimethylsilyl acetonitrile is known to react with benzaldehydes to form the first intermediate shown.[37, 38]  Aryl Grignard formation (which tolerates cyano groups)[39] followed by quenching and hydrolysis with trimethyl borate gives the second intermediate.  This can be converted to the benzylic bromide using the procedure reported by Hattori et al.[40]  Only mild base ($K_3PO_4$) is required.  This scheme is clearly the most elaborate of the three but is included as a backup and to illustrate the range of anion equivalents that could be potentially employed in this polymer synthesis.

**Scheme IX.**
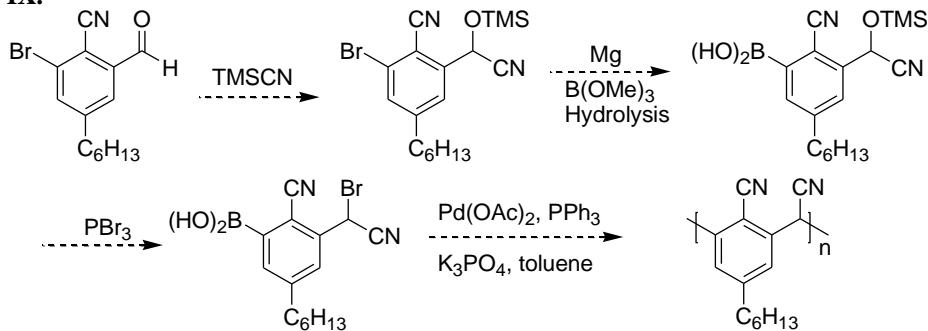


## 2    Synthesis, cyclization, tautomerization and characterization of a series of model oligomers

**Scheme X**



97 %

73 %

R = CH₃, 75%
R = C(CH₃)₃, 78%
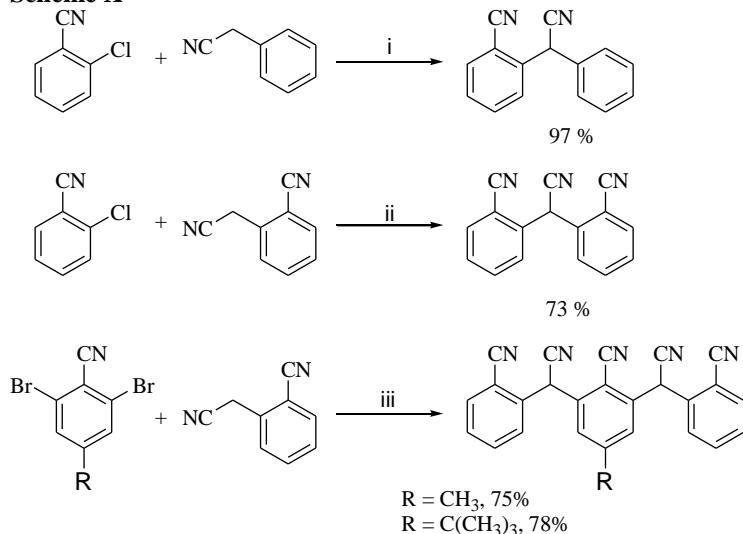
i) KO*t*Bu, DMF, rt. 3h; ii) KO*t*Bu, DMF 70 °C, 18h; iii) 5 eq. *o*-cyano benzyl nitrile, Pd(OAc)₂, BINAP, KO*t*Bu, toluene, 90 °C, 20h.
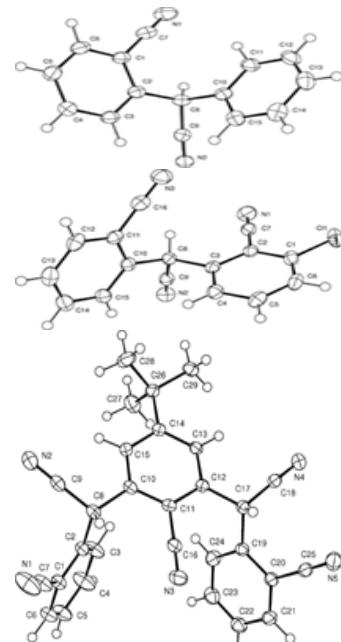
**Figure 2.  ORTEP diagrams of the three molecules prepared in Scheme X.**

### 2.1    Synthesis of model oligomer precursors

We have prepared oligomer precursors as shown in Scheme X.  The first two molecules could be prepared via nucleophilic aromatic substitution.  Preparation of the penta-cyano derivatives was accomplished via palladium-mediated substitution.[41]  These molecules have been fully characterized including via X-ray crystallography (Figure 2).

### 2.2    Acid catalyzed cyclization and spontaneous tautomerization of model oligomer precursors

These oligomers could then be converted to cyclized products (Scheme XI) in which the benzylic CH groups were found to tautomerize to NH.  This process results in entirely aromatic rings.  Acid-catalyzed monocyclizations of o-cyanobenyl benzonitrile derivatives to form isoquinolines have been reported.[42-47]  This methodology has not, however been shown to extend

to the cascade cyclization/tautomerizations illustrated here. This tautomerization obviates the need for subsequent oxidation to aromatize the rings. Scheme XI also illustrates that the bromine groups can be removed reductively using sodium borohydride in combination with palladium on carbon. This removal changes the photophysical properties of the molecules substantially as will be illustrated below. To date, we need to reproduce the yield on the cyclization of the longest oligomers (**3b** and **4b**). We have characterized the molecules fully including via x-ray crystallography (Figure 3). Both are relatively planar which is key to their extended conjugation. During the crystallization of **3b** in the presence of HBr, the terminal amino group underwent nucleophilic aromatic substitution with bromide anion to give the terminal dibromide (**3c**). Nevertheless, the structure indicates that a fully cyclized, 7 ring compound can be prepared.

**Scheme XI**
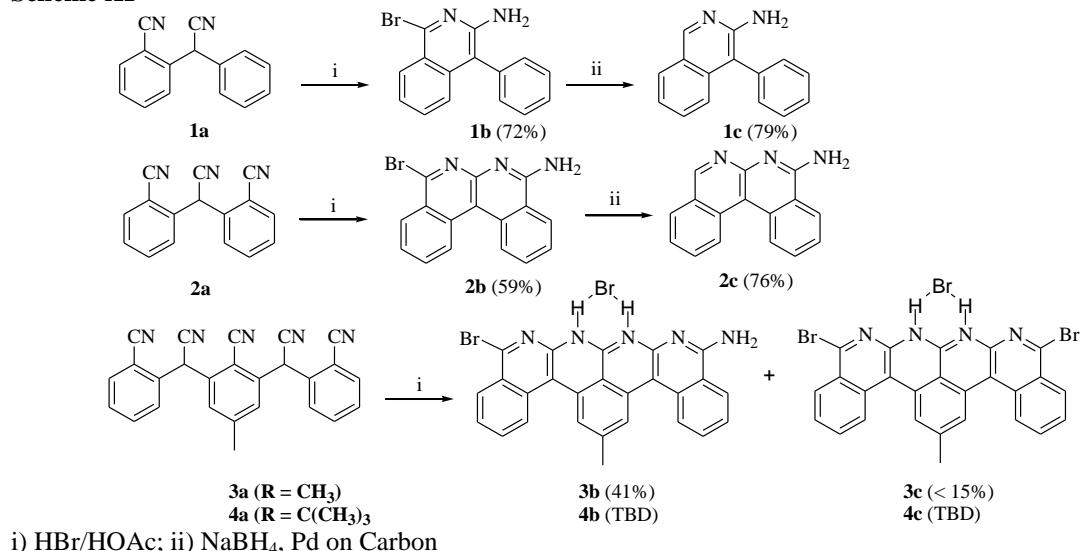


i) HBr/HOAc; ii) NaBH$_4$, Pd on Carbon
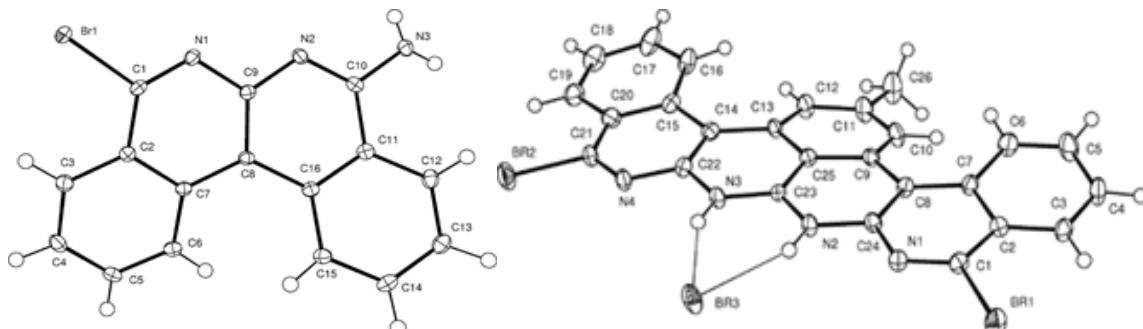


**Figure 3. ORTEP diagrams of 2b and 3c.**

## 2.3    *Measurement of spectroscopic properties of oligomers*

The absorbance and fluorescence properties of cyclized molecules have been measured. Removal of the bromide does not change the absorbance appreciably, but increases the fluorescence quantum yield dramatically (Figure 4). Quantum yield is directly relevant in the performance of any type of light emitting device. We are currently repeating measurements of the absorbance/fluorescence of **3b** and **4b**, making sure that both the free base and hydrobromide salts of these compounds are correctly characterized.
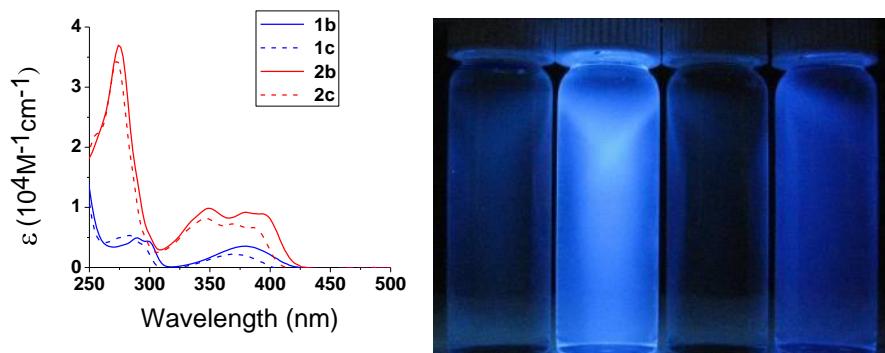
| | 1b | 1c | 2b | 2c |
|---|---|---|---|---|
| Φ | 0.02 | 0.87 | 0.03 | 0.15 |

**Figure 4. (Left) Ultraviolet visible absorption spectra and (right) emission of 1b, 1c, 2b and 2c. Calculated fluorescence quantum yields (Φ) are given below each sample.**

## 2.4 An easily synthesized, efficient mercury ion sensor: Selective binding of $Hg^{2+}$ to cyclized oligomer

The intense fluorescence of some of these compounds coupled with the available amine and pyridyl groups prompted us to explore their cation binding properties. In a broad sense, such investigations provide fundamental information about how the spectroscopic and electronic properties of these molecules can be tuned. There is a more narrowly focused application of merit as well. That is in the detection of heavy metal ions. The mercury ion is of particular interest because of it is widely found as an environmental pollutant and it is highly toxic, causing wide variety of damage to kidney, digestive, and neurological systems.[48, 49] Recently developed mercury sensing assemblies include those based on aggregation of nanoparticles,[50, 51] those based on conformational changes of conjugated polymers,[52] and those based on organic dye based sensors.[49, 53-62] While sensor assemblies of the first two types often have the advantage of lower detection limit, their applications are often highly constrained to operation under only specific conditions including but not limited to, temperature, pH, and presence of other salts. In contrast, organic dye based sensors are generally much more tolerant of different experimental conditions. However, despite a very wide range of organic dye based mercury sensors that have been reported, a survey of them indicated one or several disadvantages of each: low binding constant; poor sensitivity and/or selectivity; and poor solubility in aqueous medium. Most notable, however, is the complexity of their synthesis. Molecule **2c** (Scheme XI) is synthesized in three simple steps. Moreover, this synthesis is easily tailored to make derivatives with different solubilities. Thus, we explored this molecule as a potential sensor.

Indeed, molecule **2c** interacted selectively with mercuric ion as evidenced by both its absorbance and fluorescence spectra Figure 5. A Beneski-Hildebrand plot gave a binding constant $K_a$ of **2c** to $Hg^{2+}$ of 12000.[63] The next tightest binding (to $Zn^{2+}$) is one and a half orders of magnitude lower ($K_a = 660$). $K_a$ values for binding to all other cations investigated was too small to be measured (< 100). A Job plot gave a 1:1 binding of mercuric ion to complex.[64] Binding to commercially available 2-aminopyridine has not been reported in the literature. We measured this binding constant at only $K_a = 360$. Thus, the extended conjugation of **2c** appears to influence the strength of binding. The binding constant of **2c** with mercuric ion is among the largest reported for an organic dye. Coupled with its relative ease of synthesis and

derivatization, this side exploration may yield a useful application for this chemistry apart from those originally envisioned. This work is being submitted for publication.
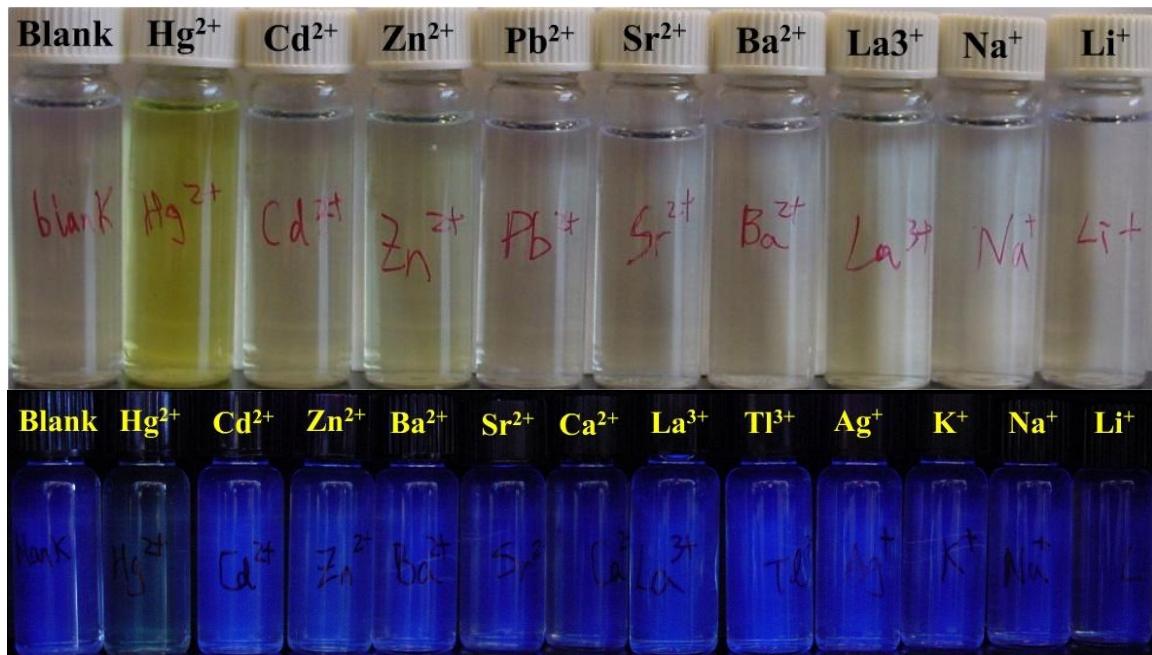


**Figure 5. Color changes and fluorescence quenching (under UV light) when 2c binds to Hg$^{2+}$ ion, compared with binding to other cations. (top) 2mM 2c with 2mM different metal cations under day light; (bottom) 0.1mM 2c with 0.1mM different metal cations under UV lamp.**

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