Stony Brook University

Topochemical Polymerization of Dibromobutadiyne and Diiodobutadiyne and Post-polymerization Attempts

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Hongjian Jin

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Abstract of the Dissertation

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All-carbon conjugated materials, the high electron-rich system, have attracted great interest for their outstanding electronic and optical properties. As a potential alternative, polydiacetylenes are also highly unsaturated and conjugated, considering as “tunable” carbon rich materials. In this work, diiodobutadiyne can be aligned in an ordered way in solid state with help of bis(pyridyl)oxalamides which are self-organized by hydrogen bond. Although diiodobutadiyne cannot polymerize at ambient condition, possibly due to spatial strain between host and

guest. We were able to polymerize it under high pressure via diamond anvil cell using *in-situ* Raman to monitor the polymerization process. Confirmed by X-ray diffraction analysis, a single crystal to single crystal transformation was obtained successfully. Dibromobutadiyne is an extremely unstable compound which could decompose, even explode at room temperature. By host-guest strategy, dibromobutadiyne formed cocrystal with bis(cyano)oxalamides at low temperature (-18°C). X-ray structure of one cocrystal was obtained in which the monomer was partially polymerized. In another cocrystal, monomer fully polymerized to afford polydibromodiacetylene (PBDA). Washing the cocrystal with solvents such as dichloromethane, THF and methanol, polymer was isolated successfully. Raman and ^{13}C SS-NMR spectrum confirmed the major presence of PBDA. Later, we tried a series of post-polymerization reactions in order to modify PBDA. Using trans-dibromoalkenes as model compounds, we tried Sonogashira and Suzuki cross coupling reactions. By alternating model compounds and reaction conditions, we got few positive results and applied the same conditions on PBDA in cocrystal and isolated PBDA as well. Although these attempts are unsuccessful, they provide a novel method of controllable synthetic pathway for derivatives of polydiacetylenes.

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I dedicate this dissertation to my parents and wife, for the continuous love, support and encouragement. I am fortunate to have you in my life.

Description of my thesis to general audience

There are 3 projects in my thesis.

In the first project, pressure is used as a method to polymerize an explosive monomer. Diiodobutadiyne (simplified as C_4I_2) is a linear molecule with central carbon-carbon triple bonds and iodine atoms on both ends. C_4I_2 is very unstable and shock explosive at room temperature. However, if C_4I_2 can form an ordered polymer, the new material may have good electronic and optical properties.

The Goroff group formed cocrystals which are crystalline structures composed of two or more components between C_4I_2 and host molecules. However, in some cocrystals C_4I_2 did not polymerize due to its spatial arrangement was not good enough. Under high pressure, C_4I_2 was able to form a polymer – polydiiododiacetylene (simplified as PIDA). The previous experiment indicated C_4I_2 could polymerize under high pressure, but the 3D structure of PIDA was not obtained. In our new experiment, we were able to obtain its 3D structure. Further analysis of the structure gave us a better understanding of the structural change in the crystal before and after polymerization at high pressure.

After PIDA was synthesized, previous members of the Goroff group tried to isolate it to explore its potential applications. Liang Luo and Daniel Resch did extensive research on this system. However, experimental results showed that the isolated

PIDA is very unstable, making its further application difficult. Attempts to convert PIDA into other stable compounds also were difficult. PIDA decomposes rapidly under a wide range of chemical conditions.

Based on additional experiments, the instability of PIDA is likely the result of the weak carbon-iodine bonds in the polymer. To prevent the decomposition, bromine was used instead. Dibromobutadiyne (simplified as C_4Br_2) was prepared.

Compared with C_4I_2, the molecule C_4Br_2 is much more unstable. It is reported to decompose at 0 °C and explodes at room temperature. It can be kept stable in dark solution below -30 °C. In order to make a new polymer, we needed to form a new cocrystal between C_4Br_2 and a host molecule. We tried many experiments using different hosts under different temperatures. Finally, C_4Br_2 formed 2 cocrystals.. In one cocrystal, C_4Br_2 did not fully polymerize Some of the C_4Br_2 molecules formed short-chain polymers and some of the C_4Br_2 remained unreacted. In the other cocrystal, most of the C_4Br_2 monomers formed polymer and the new polymer, polydibromodiacetylene (simplified as PBDA), was isolated successfully.

The successful preparation of PBDA gave us great courage. The isolated PBDA was tested and found to be stable under many conditions. Our next goal was to convert PBDA into other polymers by chemical reactions. Small molecules which have similar structure as PBDA were prepared to simulate the reactivity of PBDA.

To find a best reaction condition for PBDA, a series of experiments were tried on small molecules. Most of the results were not good. In a few reactions, small molecules reacted to afford the desired products. We used the same conditions on PBDA, but it did not react as expected. Although PBDA is relatively stable, it still decomposes at high temperature (> 60 °C). Many catalysts and reaction conditions were tried. The polymer still did not react well. We are still exploring new pathways to convert PBDA into a variety of new polymers.

Chapter 1 Introduction

1.1 Carbon-rich conjugated material

Polyacetylene is well known for its outstanding electronic and optical property. Hideki Shirakawa, Alan Heeger and Alan MacDiarmid were awarded Nobel Prize in 2000 for their pioneer work on polyacetylene.[1] Conjugated carbon-rich materials, which polyacetylene belongs to, have also attracted great interest and attention. Conjugated polymers are organic macromolecules with alternating single-, double- or triple- bonds. The distinct feature is determined by the quasi-infinite π-electrons across the backbone. The unsaturated π system endows them great electrical conductivity and optical properties.

Although polyacetylene has good physical properties, its insolubility prevents further industrial application. There are many other conjugated polymers which have similar or better physical properties than polyacetylene and more soluble. Some of them have been widely used into organic solar cells,[2] molecular wires[3] and chemical sensors.[4] Classic conjugated polymers are listed below. (Fig. 1.1)

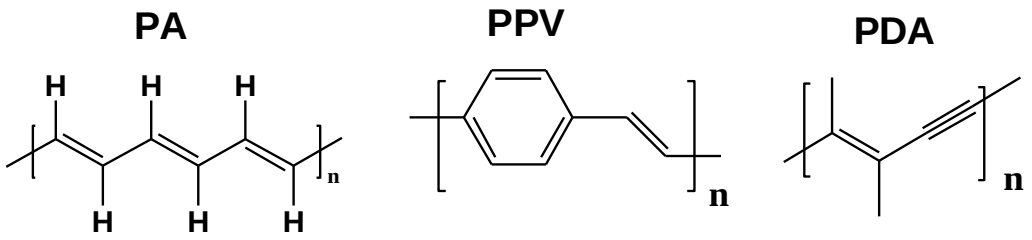

Figure 1.1 Conjugated carbon-rich materials.

It is known that the band gap between HOMO and LUMO determines the conductivity of materials. In semi-conductor, HOMO is occupied and LUMO is not. Under certain conditions, excitation could make one electron in HOMO jump into LUMO and thus make it conductive. In insulator, the energy band gap is too large for electron to jump even by excitation. For semi-conductive organic conjugated polymer, the π-electrons in HOMO can be excited to the π∗ LUMO. The ease of excitation depends on the structure.[5]

Taking polythiophene as an example, calculated by Mullekom, Meijer and coworkers, the electrical conductivity of conjugated polymer is determined by the number of repeat units.[6] (Fig. 1.2) As the number increases, the degree of conjugation increases as well. Less energy is required for excitation between HOMO and LUMO, meaning better conductivity.

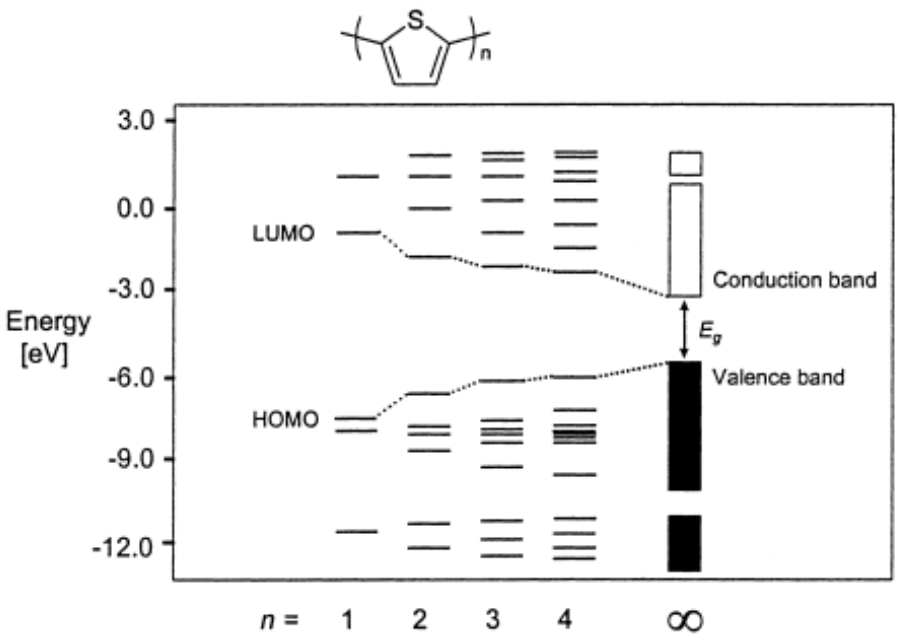

Figure 1.2 Energy gap of HOMO and LUMO of polythiophene[6]

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1.2 Synthetic background and application

Conjugated polymers have been widely used in organic solar cells. Organic solar cells have many advantages over traditional silicon-based ones. They are low-cost, flexible and light weight. It is much easier and cheaper to prepare large surface solar cells using conjugated polymers than silicon-based ones. Although the energy conversion efficiency of organic solar cell is still lower than silicon-based one, scientists continually explore new conjugated materials for better performance.

Among these polymers, poly(3-hexylthiophene-2,5-diyl) (P3HT) has been widely applied into organic solar cells as an electron donor.

P3HT is one of the most-studied materials for bulk-heterojunction organic solar cells. In bulk-heterojunction solar cells, the organic layer was randomly mixed with donor and acceptor.[7] (Fig. 1.3) Glass layer provides a substrate for deposition. ITO and aluminum layers are electrodes. The layer of poly(ethylene-dioxythiophene) doped with polystyrenesulfonic acid (PEDOT:PSS) helps the separation of positive charges and electrons. The active layer consists of a mixture of P3HT and Phenyl-C61-butyric acid methyl ester (PCBM). P3HT, the conjugated polymer, works as electron donor and PCBM works as electron acceptor. The overall efficiency of P3HT based organic solar cell is up to 4% conversion rate.[8]

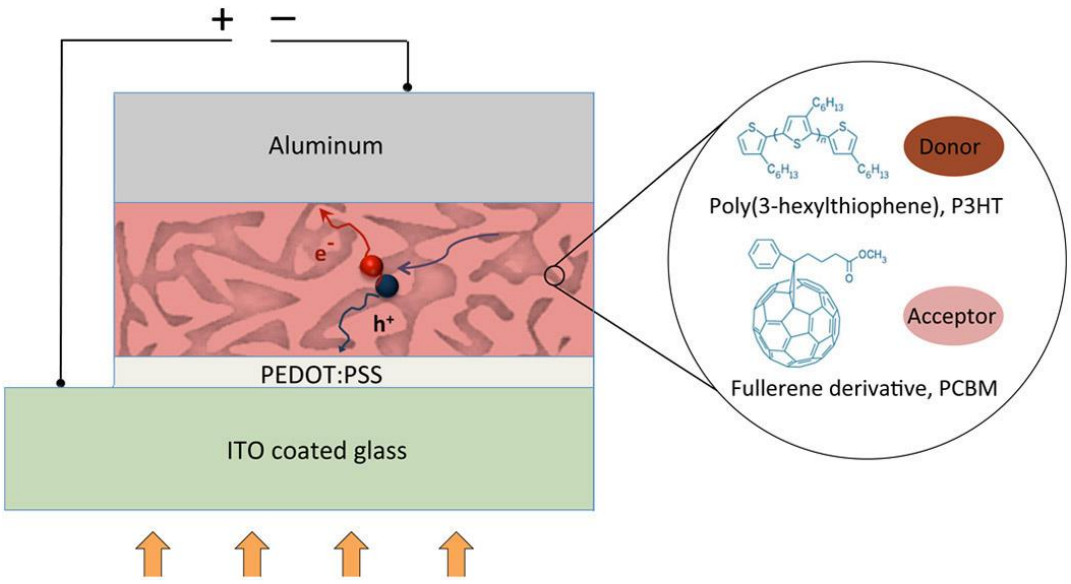
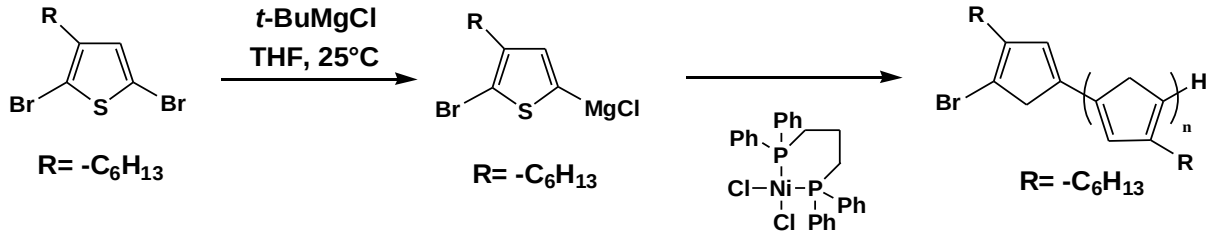


Figure 1.3 P3HT/PCBM heterojunction organic solar cell[7]

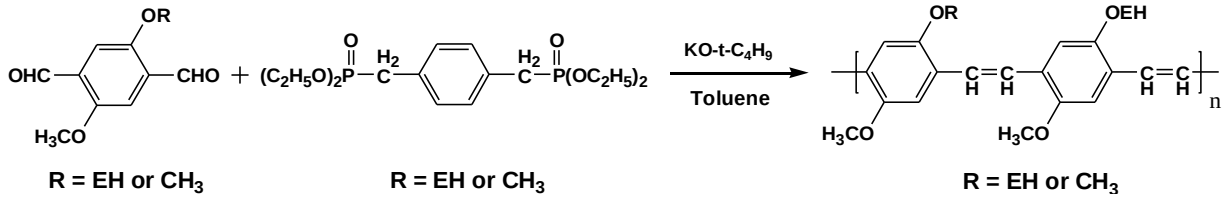
There are many synthetic routes for P3HT and its derivatives. Most of them are based on metal-catalyzed condensation polymerization. Here I introduce a reported solution based metal-catalyzed polymerization method.

The preferred method for P3HT and derivatives is Grignard polymerization. 2,5-dibromo-3-hexylthiopene is mixed with one equivalent of alkylmagnesium chloride to form a monosubstituted Grignard monomer. By Ni(II) catalyst formed in solution, the polymerization was proceeded to afford desire products.[9] (Scheme 1.1)



Scheme 1.1 Synthesis of P3HT[9]

Poly(p-phenylene vinylene) (PPV) is another conductive conjugated polymer for organic photovoltaic devices. Synthetic methods of PPV and derivatives include Suzuki cross coupling reaction,[10] dehydrohalogenation[11] and Wittig-type olefination x.[12] Here is one example.(Scheme 1.2)



Scheme 1.2 Preparation of PPV[12]

1.3 Host-Guest Strategy for 1.4-Topochemical Polymerization

In 1969, Wegner first discovered the 1,4-topochemical polymerization of 2.4-hexadiyn-1.6-diols derivatives in crystalline state.[13] 5 years later, based on Wegner's observations, Baughman calculated an ideal criteria for topochemical polymerization of diyne.[14] When monomers are aligned in an ordered way with a distance commensurate with the repeat distance in the desired polymer, they will polymerize. To induce a 1,4-polymerization of diynes, the spatial requirement should be a repeat distance of 4.9 – 5.0 Å and a title angle of 45 °. (Fig. 1.4)

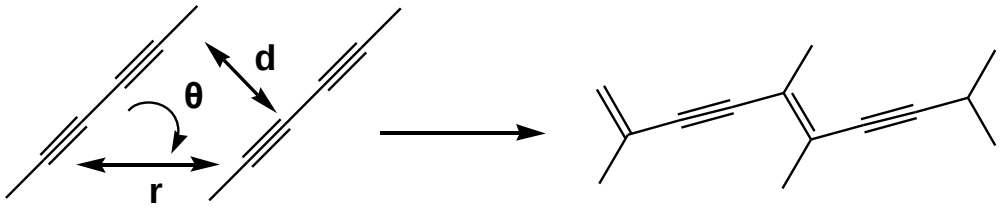


Figure 1.4 Alignment of diynes for topochemical polymerization. Optimal values for 1,4-polymerization are r = 4.9-5.0 Å, θ= 45 °, d = 3.5 Å.

Most of diynes cannot align themselves into the desired way for 1,4-polymerization. Lauher and Fowler created a host-guest strategy to solve this

problem. Host with functional groups can reliably self-assemble into one-dimensional hydrogen-bonded network. Guest, a di-substituted diyne, hydrogen bonds to host and gets aligned as well. In order to find proper combination, they did substantial amount of works.

First, a series of urea biscarboxylic, urea bispyridyl, oxalamide biscaboxylic, oxalamide bispyridyl and their derivatives were designed, synthesized and characterized by single-crystal X-ray diffraction analysis. The central urea or oxalamide could each self-assemble into one-dimensional network. The terminal carbonxylic or pyridyl could hydrogen bond to different diynes to form two-dimensional networks. Below are representative compounds.[15] (Fig 1.5)

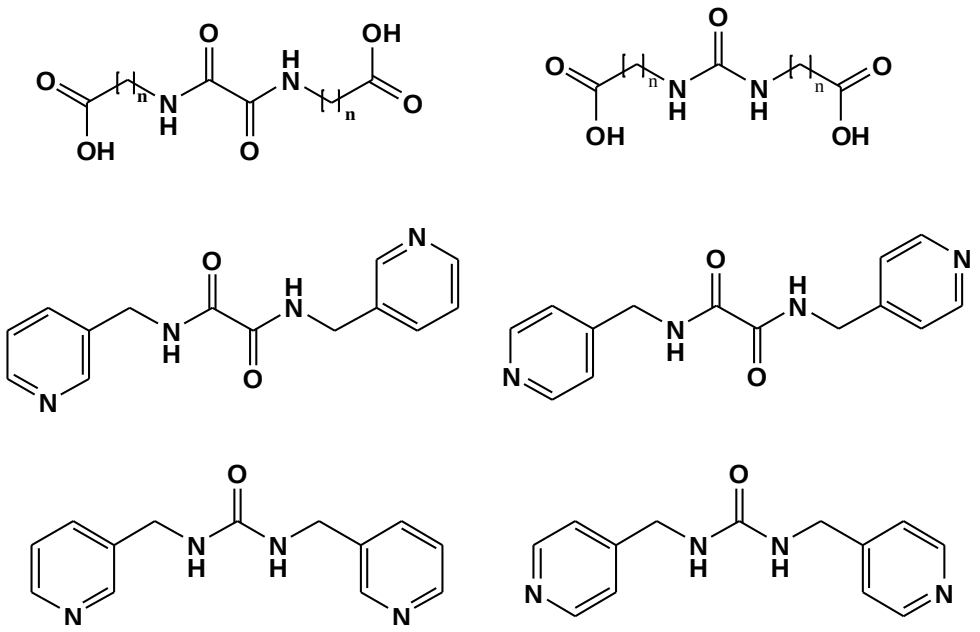


Figure 1.5 Hosts compounds[15]

These compounds were used as hosts to build two-dimensional networks. Guests which contain central diynes and two terminal functional groups could bond to hosts and get aligned in a desired way. By choosing different hosts and guests, diyne can be well aligned and quickly polymerize into polydiacetylene.[16] (Fig. 1.6)

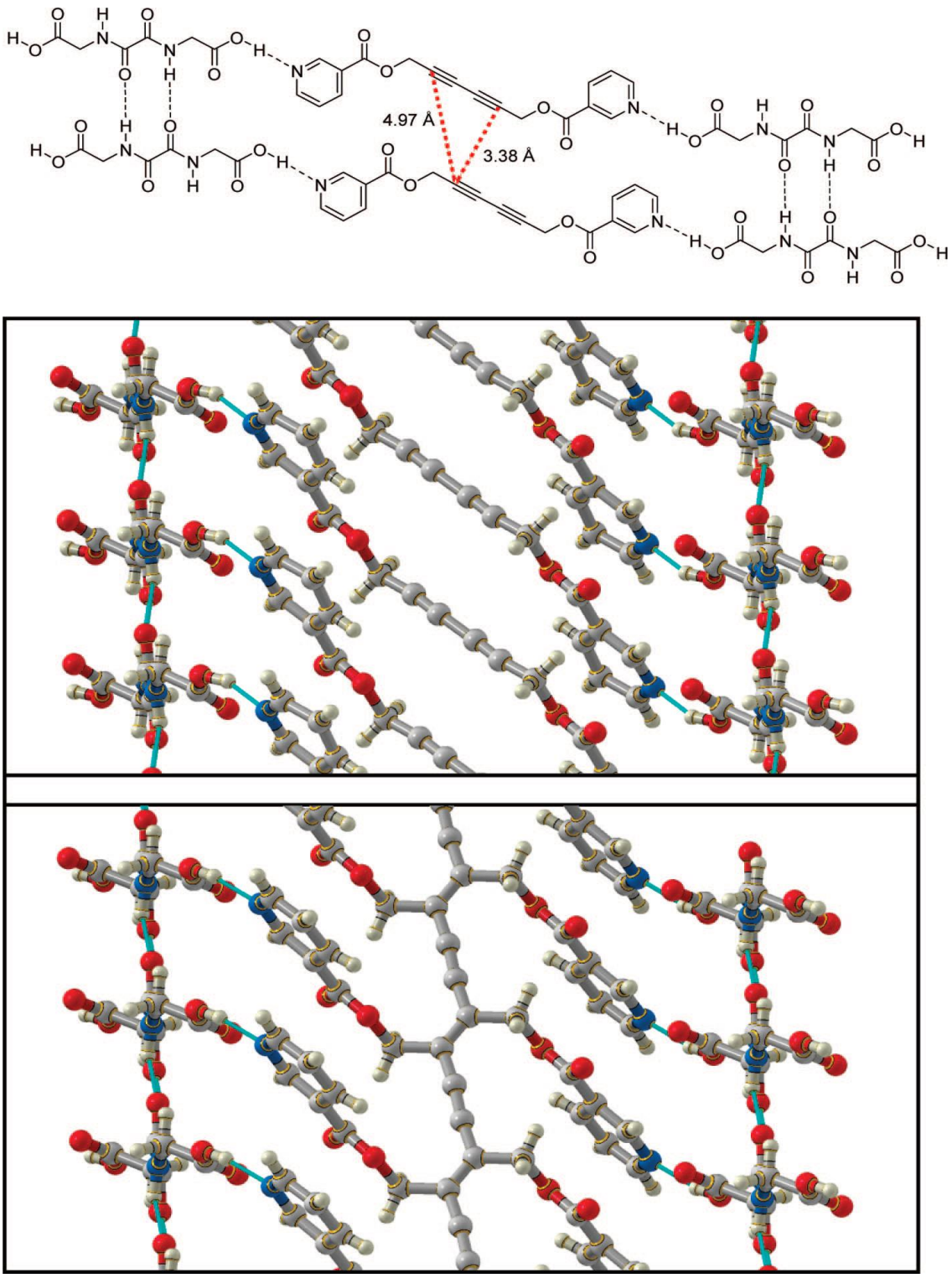


Figure 1.6 Single-crystal-to-single-crystal diyne polymerization.[16] Red – oxygen, blue - nitrogen, grey – carbon, white – hydrogen

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1.4 The preparation of polydiiodobutadiyne (PIDA)

The Goroff group has been working on synthesizing the simplest polydiacetylene. Using it as an intermediate to prepare a variety of polydiacetylenes or eliminating it to afford carbyne is our original final target. To prepare the simplest polydiacetylene, we incorporated host and guest strategy with halogen bonding concept.

Halogen bonding is the non-covalent interaction between Lewis base and Lewis acid.[17] It is a parallel world to hydrogen bonding which has been widely used in material chemistry and biochemistry.

The halogen bonding was first described by Guthrie in 1896. He observed the formation of $NH_3 \cdots I_2$ complex.[18] Later, crystallographic studies by Hassel provided a deeply understanding of halogen bonding.[19]

Halogen atoms are highly polarizable. When halogen atoms are bonded to electron withdrawing group, they will be electron deficient, which could easily form non-covalent interaction with Lewis base. More importantly, since halogen bonding is the interaction between electron deficient and electron rich functional groups, they are highly directional. Most of the bonding angles are between 160° and 180°. Among halogen atoms, the relative bonding strength is I > Br > Cl > F.[17] In most of the case, there is no halogen bonding in fluorine.[20]

Aiwu Sun and Liang Luo combined the concept of host-guest strategy with halogen bonding. They prepared a series of host molecules (**3** - **7**), which have nitrile or pyridine functional groups as the halogen bonding acceptors, and diiodobutadiyne **1** as the halogen bonding donor.[21] (Fig. 1.7)

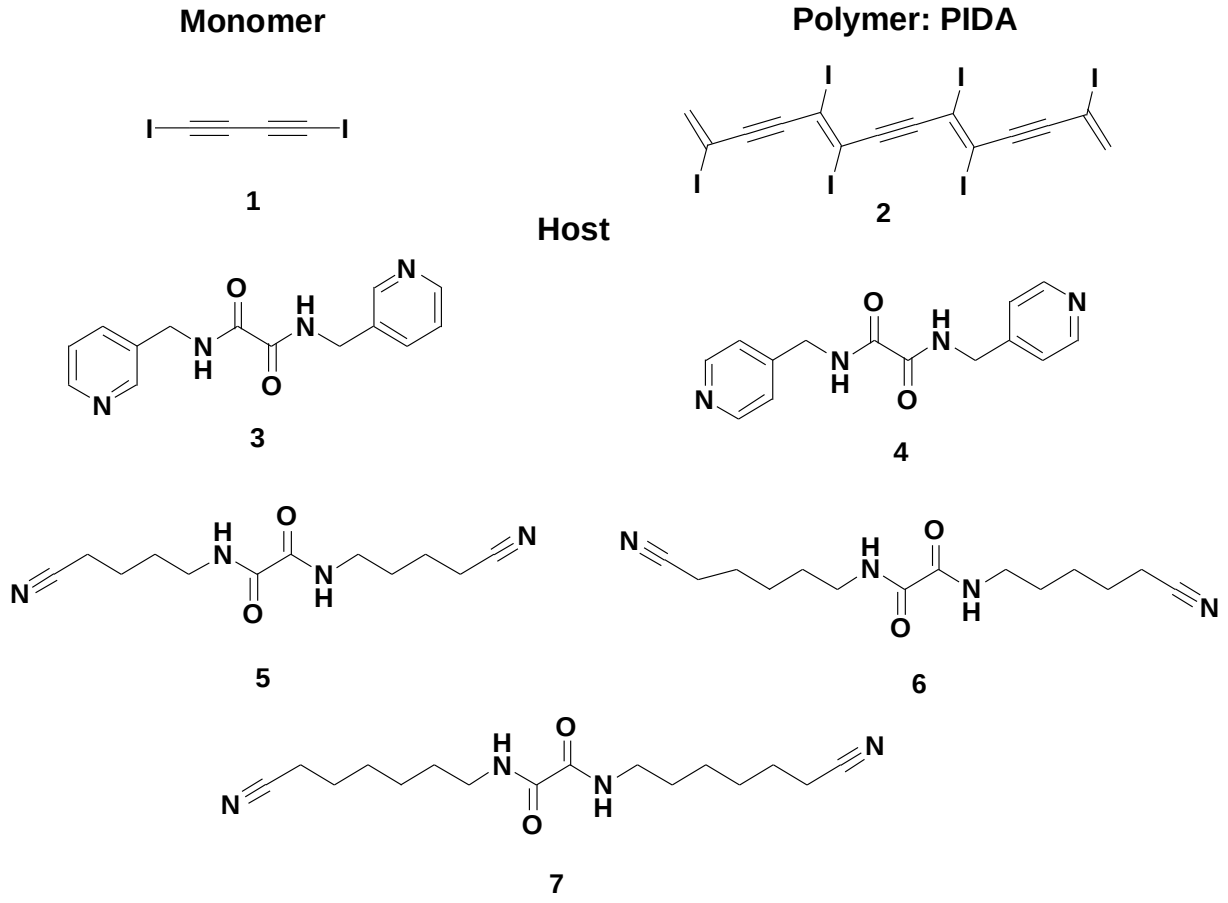

Figure 1.7 Diiodobutadiyne (**1**), Polydiiodobutadiyne (**2**) and hosts (**3-7**).[21]

Pyridine is a stronger Lewis base than nitrile, so host **3** is more likely to form cocrystal with **1** than host **5**, **6** and **7**. On the other hand, host **5**, **6** and **7** have

longer alkyl chains comparing to host **3** which are more flexible to be commensurate with steric change of monomer upon polymerization.

After numerous attempts, hosts **3** and **6** were able to form cocrystal with monomer **1** separately. However, monomer **1** in cocrystal could not polymerize. Host **5** and **7** each also formed cocrystals with monomer 1, in which monomer **1** quickly polymerizes into polydiiododiacetylene (PIDA).(Fig. 1.8) PIDA is the first reported single atom side-chain polydiacetylene.[22]

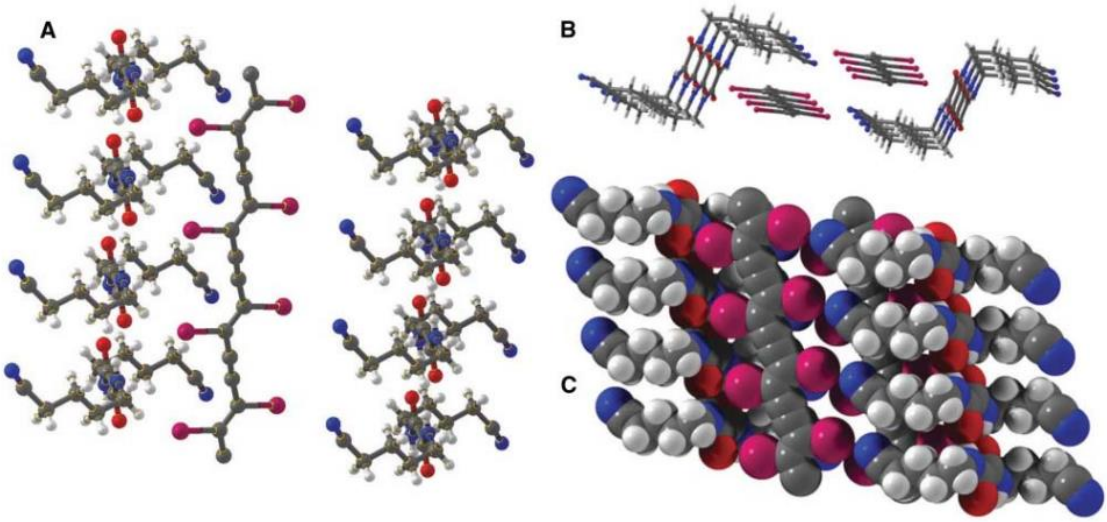

Figure 1.8 View of PIDA in different angles.[22]

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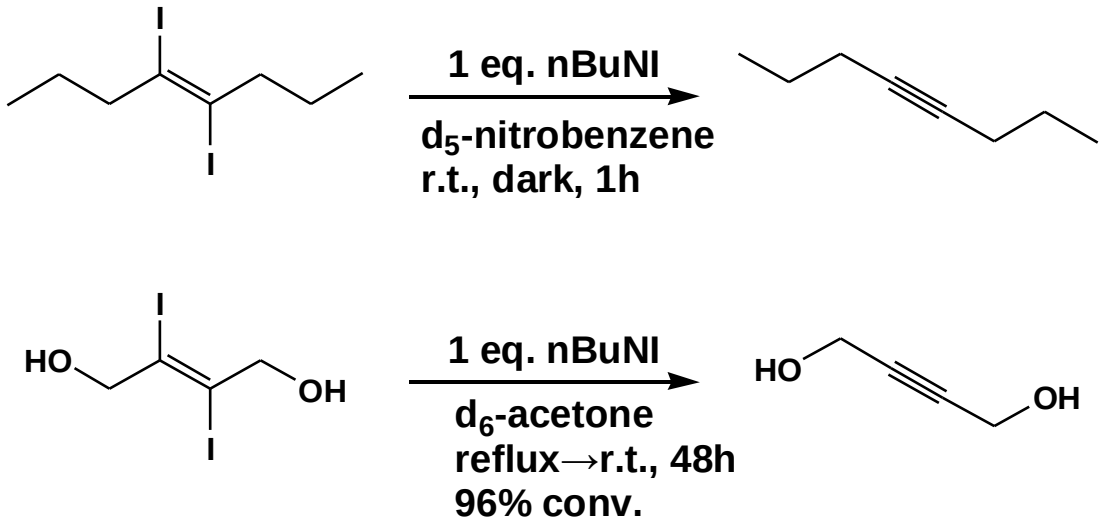
Although PIDA cocrystal was successfully prepared, isolation and post-polymerization reaction attempts were not successful.[23] Research by Liang Luo

and coworkers demonstrates that PIDA is very difficult to stabilize once isolated from cocrystals.[24]

PIDA is very reactive. The low Raman intensity of isolated PIDA compared to PIDA cocrystal suggests it decomposes significantly during the isolation proecss. And the isolated PIDA is very unstable and shock explosive. Once isolated PIDA gets mixed with different bases, it got eliminated immediately to afford a random cross-linked material.[23b] Model compound reaction also showed similar results.[23a] (Scheme 1.3)



Scheme 1.3 Elimination of iodine from trans-diiodoalkene[23a]

As we understand, the problem comes from the highly polarized iodine. When attacked by any Lewis base, the highly polarized iodine in the PIDA was prone to

leave to afford an unsaturated string, which can easily random polymerize with nearby strings.

Hence we consider using a weaker halogen bond donor instead. Bromine is a good alternative. Unlike chlorine which hardly forms halogen bond, bromine was reported to form halogen bond, but weaker than iodine. Also bromine is less polarizable which means more stable than iodine. Once polydibromobutadiyne formed, it will be easy to get isolated and stabilized to undergo post-polymerization reactions.

Chapter 2 Pressure induced single-crystal-to-single-crystal transformation

2.1 Background

Diiodobutadiyne **1** forms cocrystals with host **3**, **4**, **5**, **6** and **7**. In **1•5** and **1•7**, it undergoes spontaneous polymerization to afford PIDA.[22, 24] While in **1•3** and **1•6**, diiodobutadiyne did not polymerize completely.[22, 25] X-ray analysis showed the repeat distance of monomer **1** in cocrystal **1•3** and **1 • 5** is 5.02 and 5.11 Å, very close to the desired distance for 1,4-topochemical polymerization. Therefore it is possible to induce polymerization under specific conditions theoretically. However, many attempts to induce polymerization such as irradiation of visible or UV lights or heating were not successful. The cocrystal either underwent partial polymerization or was increased mosaicity, preventing a clean polymerization. The steric interfere between pyridine ring and neighbor iodine appears to be the main issue. There is only one methylene between pyridine ring and central oxalamide.[25]

Pressure has been reported as a method to induce polymerization of solid-state diynes.[25-26] Diamond anvil cell (DAC) is a small device which could provide very high pressure in limited space.[27] (Fig. 2.1) It consists of two diamond anvils in which samples, ruby and compressible fluid are compressed inside. Pressure can be monitored and calibrated by the ruby whose behavior under pressure is known.

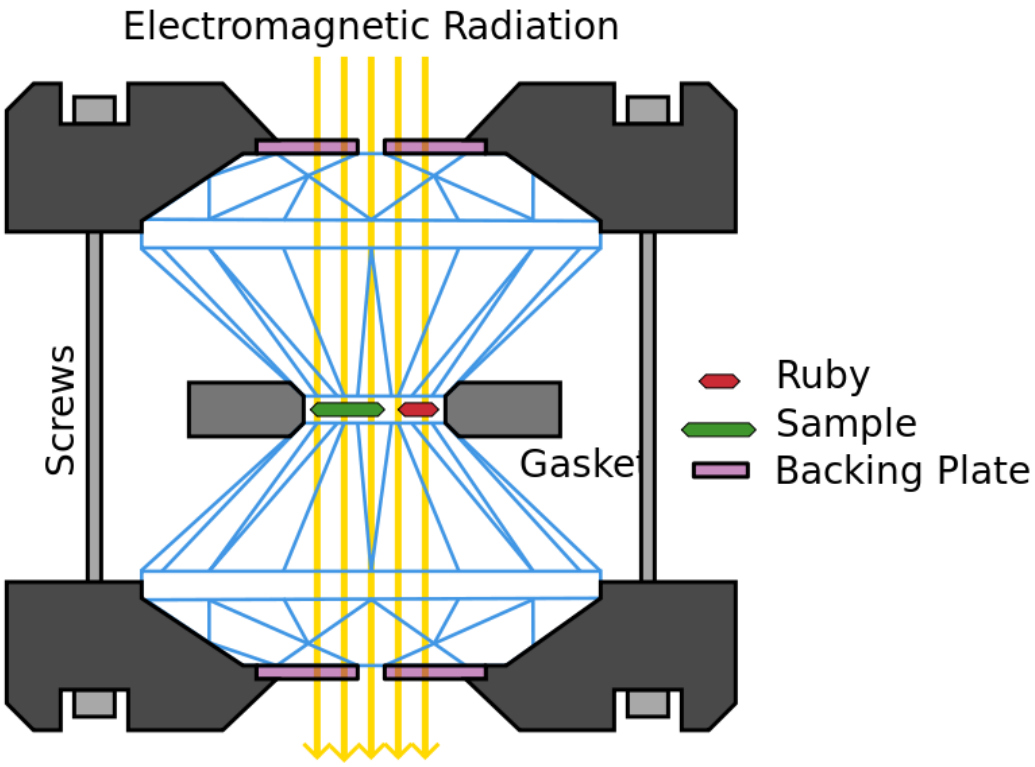


Figure 2.1 The structure of diamond anvil cell[27]

Collaborated with John Parise's group, Jeffery Webb and Christopher Wilhelm first polymerized diiodobutadiyne in cocrystal **1•3** at 3 GPa using DAC. Based on solid-state MAS NMR, the polymerization degree is 90%. However, a single crystal to single crystal transformation was not obtained.[25]

Collaborating with Anna Plonka and John Parise, our target was to obtain a single-crystal to single-crystal transformation to fully understand the polymerization process at molecular level. *In-situ* Raman microscopy makes it possible to take Raman spectrum when sample is in the DAC. It allows us to monitor the

experiment progress at high pressure. Hence we can determine the proper time to take X-ray diffraction for further analysis.

2.2 Inducing topochemical polymerization of 1•3 at high pressure

2.2.1 Cocrystal preparation

Cocrystal **1•3** and **1•5** were prepared by slow evaporation from solutions of guest and hosts (molar ratio 1:1.1) in a mixture of methanol and acetonitrile (volume ratio 1:10) at room temperature over 2 days.

2.2.2 Raman Spectroscopy

For each experiment, monomer cocrystal, a ruby chip for pressure calibration and fluorinert as a pressure-transmitting medium were loaded in a diamond anvil cell with 600 mm cullet diamonds. By measuring the optical fluorescence of ruby R1 and R2 lines, pressure inside the DAC was calculated and calibrated. As pressure increased, *in-situ* Raman had been taken at every 0.5 GPa. The maximum pressure of **1•3** cocrystal and **1•4** cocrystal in DAC is 3.5 GPa and 5.4 GPa. Produced by a 532 nm Nd:YAG laser with microscope, a ~650 nm laser beam was focused on the sample. And the scatter light was analyzed by a UHTS 300, f/4, 300 mm focal-length spectrometer, equipped with a 600 lines mm21 grating and a

thermoelectrically-cooled charge-coupled device detector. The whole experiment was done at room temperature.[28]

2.2.3 X-ray Diffraction

X-ray diffraction analysis was processed before pressure, after pressure and after polymerization to track the conversion of structure of polymer. Oxford Gemini diffractometer was used to perform the X-ray diffraction. The data was analyzed by CrysAlis Pro software. Anisotropic displacement refinement was applied to all atoms except hydrogen. And absorption correction was applied to iodine atoms. Also in the refinement pyridine ring was refined to be planar. [28]

2.3 Results and discussion

Cocrystals **1 • 3** and **1 • 4** were placed into separate DAC for high pressure experiment. For cocrystal **1•3**, the color changed as the pressure got increased, indicating the ongoing polymerization. The crystal was turned blue at 1.1 GPa and the *in-situ* Raman spectroscopy showed three peaks at 970 cm^{-1}, 1389 cm^{-1} and 2043 cm^{-1} but low Raman intensity and high fluorescent background, suggesting partial polymerization. As pressure was increased to 3.5 GPa, the crystal was turned black with metallic copper color, suggesting high degree polymerization based on our previous experience. By the *in-situ* Raman spectroscopy, the intensity

of the polymer peaks reached to a very high level.(Fig. 2.2) Monomer underwent a topochemical polymerization.[28]

With *in-situ* Raman, we were able to map the Raman intensity of surface of sample rather than a single spot or a small area. Focusing on the rectangle area in Fig 2.1A, different polymer modes of Raman images all showed homogeneous yellow color, indicating the polymerization took place throughout the cocrystal. The intensity of

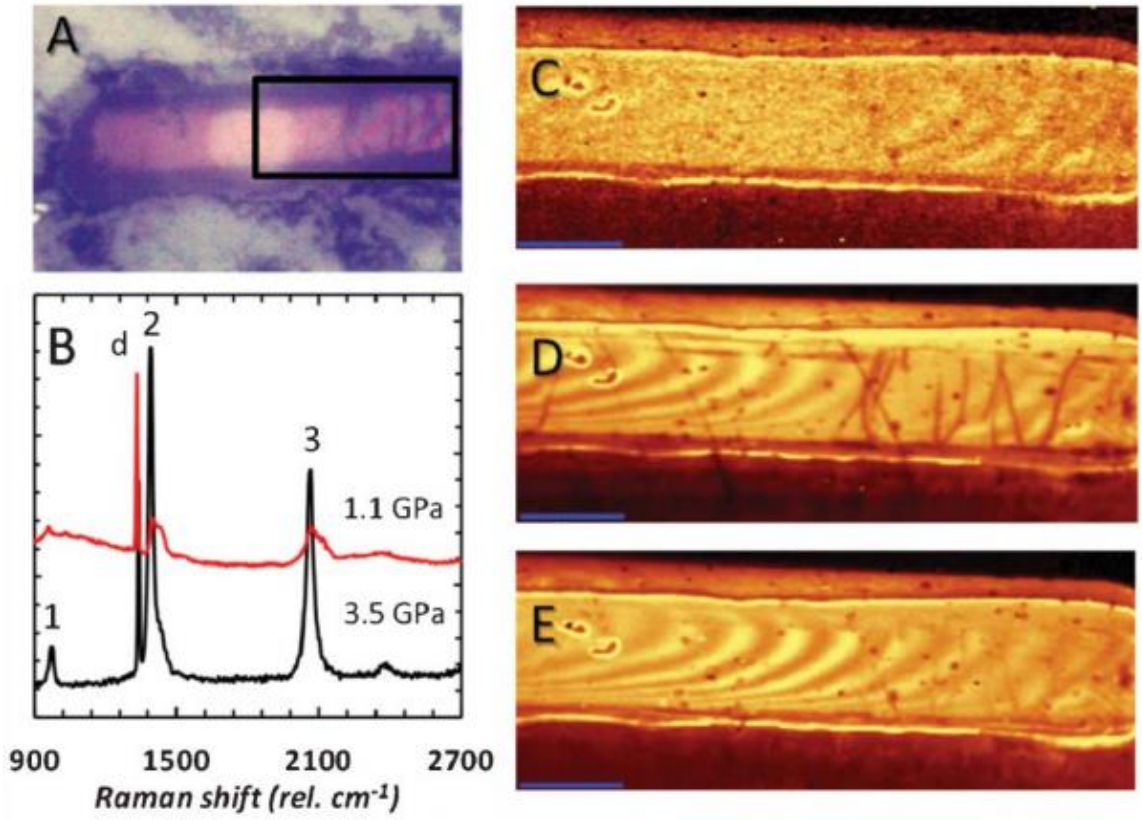


Figure 2.2 In-situ high pressure experiment on cocrystal **1•3** A) Crystal inside the DAC at 3.5 GPa. Black rectangle is the area which Raman was taken from. B) Raman spectrum at 1.1 GPa (Red) and 3.5 GPa (Black). C) First polymer mode (120–920 cm-1). D) Second polymer mode (1355–1420 cm-1). E) Third polymer mode (2000–2125 cm-1). Blue bar represents 15 mm[26]

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Raman spectroscopy of polymer peaks was increased significantly compared to the one at 1.1 GPa. X-ray diffraction of the recovered cocrystal after high pressure confirmed the full polymerization.

For **1 • 4** cocrystal, the same experiment was performed as **1 • 3** cocrystal. As pressure was increased, the color of **1 • 4** cocrystal changed. The Raman spectroscopy of the polymer modes was not prominent at 5.4 GPa. The intensity was significantly lower than the one of **1•3** cocrystal. In addition, the color of cocrystal at 5.4 GPa was not homogeneous black seen from microscope, indicating a partial polymerization of monomer. X-ray diffraction of the recovered crystal after high pressure experiment still showed primary monomer. (Fig. 2.3)

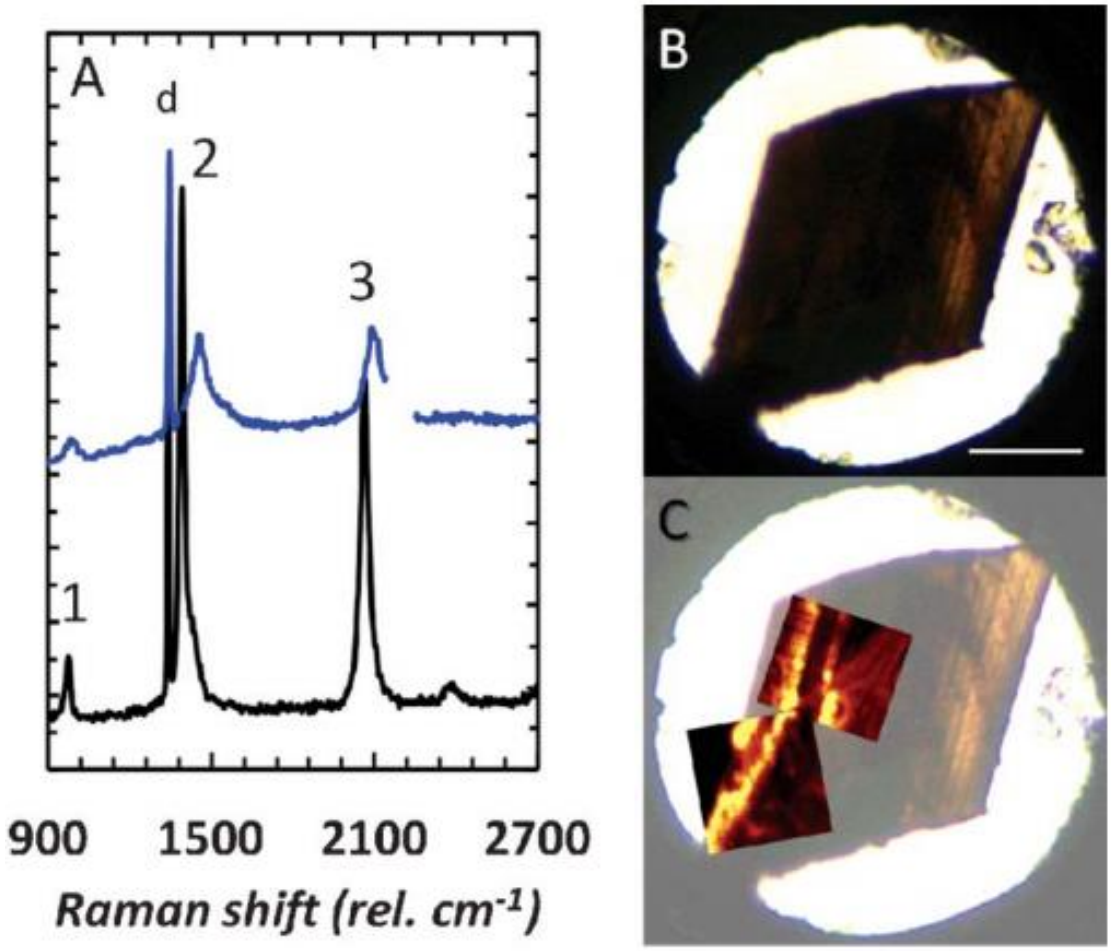

Figure 2.3 *in-situ* high pressure experiment on cocrystal **1•4**. A) Raman spectrum of cocrystal **1•4** at 5.4 GPa (Blue) and 3.5 GPa (Black), normalized to the diamond peak d. B) Cocrystal inside the DAC at 5.4 GPa, not homogenous black color. C) The same cocrystal with overlaid Raman spectrum, within polymer mode (1400 – 1600 cm^{-1}).[26]

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Structure changes before and after polymerization.

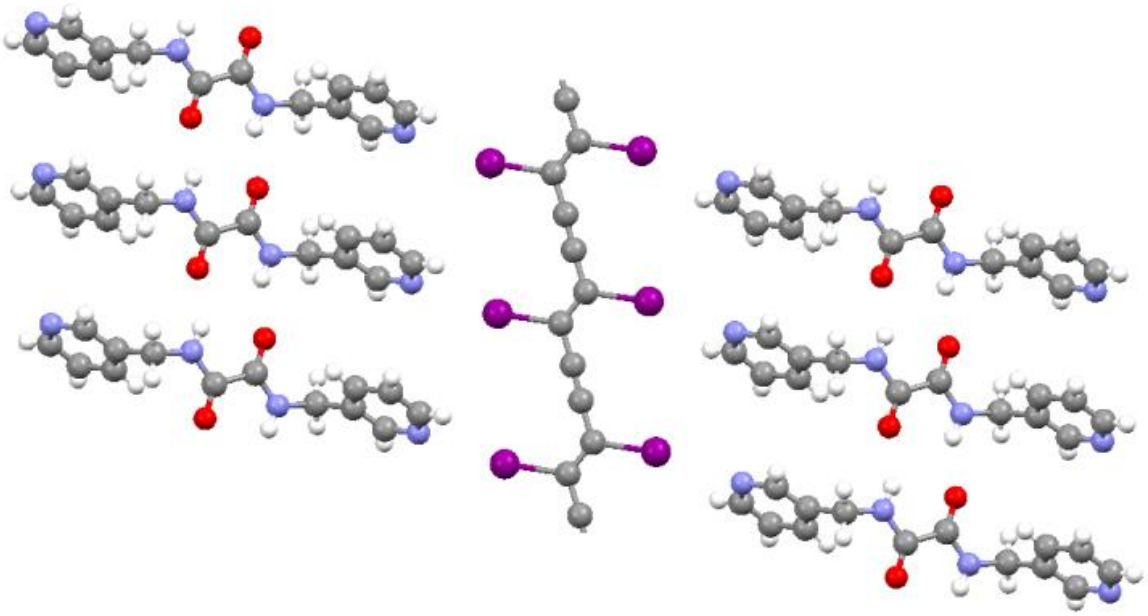

Figure 2.4 The structure of full polymerized diiodobutadiyne inside cocrystal **1•3** determined by X-ray diffraction. Purple – iodine, grey- Carbon, red – oxygen, blue – nitrogen and white – hydrogen.[26]

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X-ray diffraction analysis indicated the monomer was transformed into the polymer during high pressure experiment.(Fig. 2.4) During polymerization, the unit cell parameters changed significantly. The repeat distance in between ordered monomers is equal to *a* parameter of unit cell. Before and after polymerization, the a distance decreased from 5.11 Å to 4.93 Å, which was very similar to the one of

PIDA in cocrystal **1•5** (4.94 Å), close to the idea parameter for topochemical polymerization. Meanwhile, the *b* decreased slightly and the *c* increased from 11.78 Å to 12.28 Å, indicating a stretch along c direction and compression along *a* and *b* direction. (Fig. 2.5)

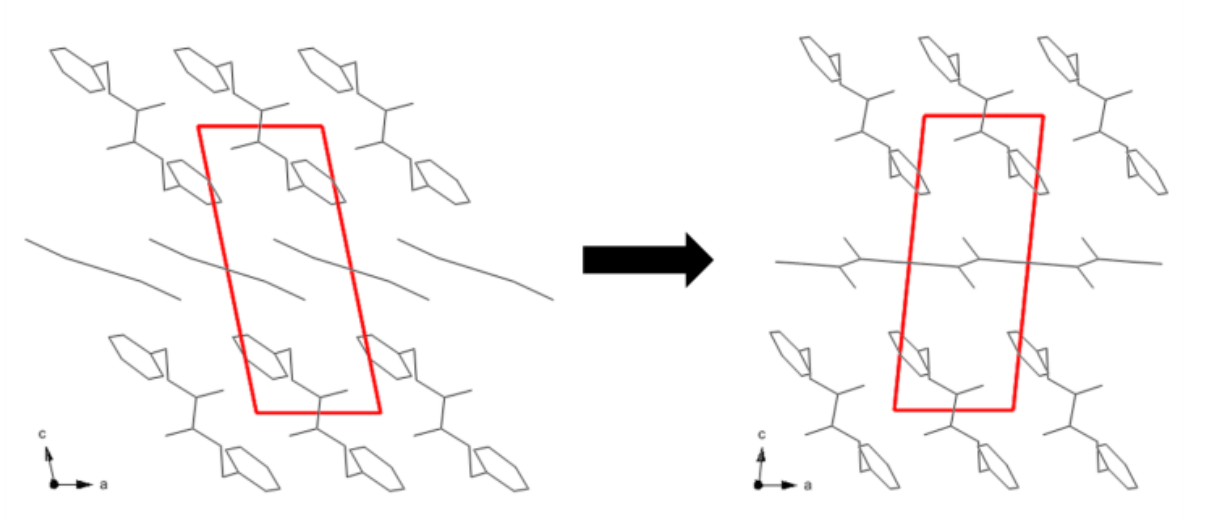

Figure 2.5 Change of unit cell before and after polymerization, 010 view which shows the significant change of β.[26]

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The unit cell angles (α, β and γ) also changed significantly. The α increased from 96.1 ° to 100.5 °, γ decreased from 103 ° to 97 °. These differences were minor changes. However, β changed from 99.6 ° to 82.9 ° which indicated a great movement of pyridine hosts in unit cell, forcing monomer became closer to each other. It was observed that the hydrogen bond length between nitrogen and nearby oxygen got shortened during polymerization. (Table 2.1)

Table 2.1 Crystallographic data and structural refinement details of **2•3** cocrystal.

Empirical formula	$C_{18}H_{14}I_2N_4O_2$
Formula weight	572.13
Collection Temperature (K)	100
Wavelength (Å)	0.71073
Space Group	$P\bar{1}$
a (Å)	4.9330(3)
b (Å)	8.4214(5)
c (Å)	12.3642(8)
α (°)	100.542(5)
β (°)	82.986(5)
γ (°)	97.144(5)
Volume (Å^3)	498.45(5)
Z	1
Calculated Density (g/cm^3)	1.906
Absorption coefficient(mm^{-1})	3.174
F(000)	272.0
Crystal size (mm)	0.15×0.05×0.03
Θ range of data collection (°)	3.83 - 26.37
Index range	$-6 \le h \le 6$, $-10 \le k \le 10$ $-15 \le l \le 15$
Collected reflections	13901
Independent reflections	2038
R_{int}	0.0794
Completeness to Θ_{max}	99.8 %
Data/ Restraints/parameter	2038/15/118
R_1(*on* F_o, $I>2\sigma(I)$)	0.0673
wR_2 (*on* F_o^2, $I> 2\sigma(I)$)	0.2064
Goodness of fit	1.050

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The other major change during polymerization is the halogen bonding which can be analyzed by N1-I1-C1 angle and N1--I1 distance.(Fig. 2.6) The angle decreased from 169.7° to 161.4° and distance increased from 2.83Å to 3.03 Å. The halogen bond gets weakened after polymerization. The movement of host and guest is unfavored for the aspect of halogen bond.

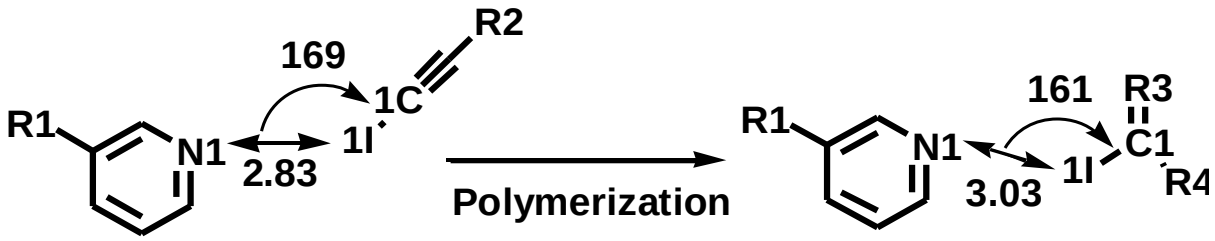


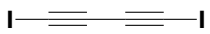
Figure 2.6 Halogen bond changes after polymerization.[26]

2.4 Summary

Diiodobutadiyne in cocrystal with bis(pyridyl)oxalamide **3** polymerized into PIDA under high pressure up to 3.5 GPa. It is the first reported pressure-induced single-crystal to single-crystal-transformation polymerization. On the other hand, diiodobutadiyne in cocrystal bis(pyridyl)oxalamide **4** partially polymerized under high pressure up to 5.4 GPa. It implies the success of polymerization depends on the initial alignment of monomer in cocrystal as well.

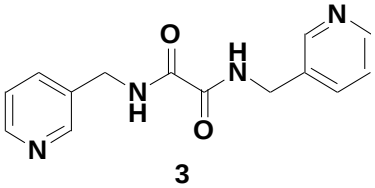
2.5 Experimental

Safety note: Diiodobutadiyne (1) is unstable at room temperature and explosive at 80 °C. To reduce risks of explosion, compound 1 was prepared only in quantities of less than 300 mg. When it was prepared, it was stored in solutions.



1

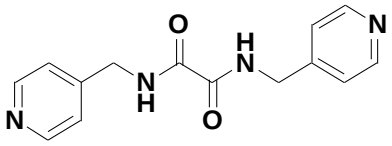
1,4-Diiodobutayine 1: Bis(trimethylsilyl)butadiyne (500 mg, 2.57 mmol) was dissolved in 200 mL acetone in a round-bottom flask which was wrapped with aluminum foil. AgNO3 (0.873 g, 5.14 mmol) and NIS (1.15g, 5.14 mmol) were added. The mixture was stirred at dark for 4 hours. Solvent was removed in *vacuo* at room temperature. A short plug (SiO_2/hexane) was used to isolate **1** as yellow solids. The product weighed 626.2 mg (81%). ^{13}C NMR (400 MHz, CDCl3) δ 79.97, -2.70.[29]



3

N,N'-bis-(3-pyridylmethyl)oxalamide **3**: 3-amine-1-pyridine (261.5 mg, 2.41 mmol) was dissolved in THF in a round-bottom flash bubbled with argon. Diethyl oxalate (168.2 mg, 1.15 mol) was added. The mixture was stirred at room

temperature overnight. Solvent was removed in *vacuo* and the crude product was recrystallized by ethanol to afford white solid. The product weighed 257.2 mg (82%).[30]



4

N,N'-bis-(4- pyridylmethyl)oxalamide **4**: 4-amine-1-pyridine (0.25g, 2.41 mmol) was dissolved in THF in a round-bottom flash filled with argon and diethyloxalate (168.2 mg, 1.15 mol) was added. The mixture was stirred at room temperature overnight. Solvent was removed in *vacuo* and the crude product was recrystallized by ethanol to afford white solid. . The product weighed 247.2 mg (79%).[15b]

Cocrystal **1·3**: A 1:1 ratio of host **3** to guest **1** (21 mg : 30 mg) were dissolved in 3 mL methanol. The mixture was subjected to sonication for 1 minute and was transferred to a test tube. The solution was centrifuged for 10 minutes and the liquid was decanted into a 50 mL crystallization dish. The dish was covered with aluminum foil which was punctured 9 holes by needle. The solution was left on benchtop for 1-2 days until the solvent evaporated off.

Cocrystal **1·4**: A 1:1 ratio of host **4** to guest **1** (21 mg, 30 mg) were dissolved in 3 mL methanol. The mixture was subjected to sonication for 1 minute and was

transferred to a test tube. The solution was centrifuged for 10 minutes and the liquid was decanted into a 50 mL crystallization dish. The dish was covered with aluminum foil which was punctured 9 holes by needle. The solution was left on benchtop for 1-2 days until the solvent evaporated off.

High-pressure Raman spectroscopy

A single crystal of monomer cocrystal and a ruby chip for pressure calibration were loaded, with fluorinert as a pressure transmitting medium, into a Merril-Basset diamond anvil cell (DAC) equipped with 600 μm cullets diamonds. Pressure was calibrated, based on measuring the optical shift of ruby R1 and R2 fluorescence lines, and was increased up to 3.5 GPa for **1·3** cocrystal and up to 5.4 GPa for **1·4** cocrystal.. Unpolarized Raman spectra were collected with a WITec alpha300R confocal microscopy system. The Raman microscope images were collected at the highest pressure for each cocrystal. A frequency-doubled Nd:YAG laser, with a wavelength of 532 nm was used as the excitation source and was focused onto the sample in the DAC with an optical microscope, producing a laser-beam size of ~650 nm at the sample. The scattered light was collected in a back-scattering geometry and analyzed by a UHTS 300, f/4, 300-mm focal-length spectrometer, equipped with a 600 lines/mm grating and a thermoelectrically-

cooled charge-coupled device detector. All measurements were taken at a room temperature. [28]

Single-crystal x-ray diffraction of polymer cocrystal

After the high pressure experiment, the PIDA cocrystal with host 3 was recovered and was mounted on a CryoLoop for single-crystal data collection. Reflections were collected at low temperature (100 K), using a four-circle kappa Oxford Gemini diffractometer equipped with an Atlas detector (λ = 0.71073 Å) with 1° □ scans. The raw intensity data were collected, integrated and corrected for absorption effects using CrysAlis PRO software. All of the non-hydrogen atoms were refined with anisotropic displacement parameters. Pyridine ring of hosts was constrained to be planar and hydrogen atoms were added in the structure using geometrical constraints.[28]

Chapter 3 Topochemical polymerization of dibromobutadiyne

3.1 Background

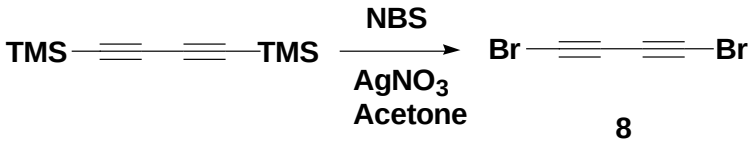
As described in chapter **1**, polydiiododiacetylene **2** is difficult to stabilize, which prevents its further functionalization. To prepare a more stable polymer which is polydibromodiacetylene, dibromobutadiyne, a very challenge compound, was used. First reported in 1930, it decomposes at 0 °C and explodes at room temperature.[31] Only in dark solution below -30 °C, it is stable. Due to its instability, further exploration of dibromobutadiyne is limited.

The most recent progress on bromodiyne was done by Frauenrath and coworkers 2 years ago. They reported a single-crystal-to-single-crystal dimerization of glycosylated bromopolyynes. It is the first reported dimerization of bromopolyynes.[32]

3.2 Synthesis of Monomer 8 and building cocrystals between dibromobutadiyne 8 and host 3-7.

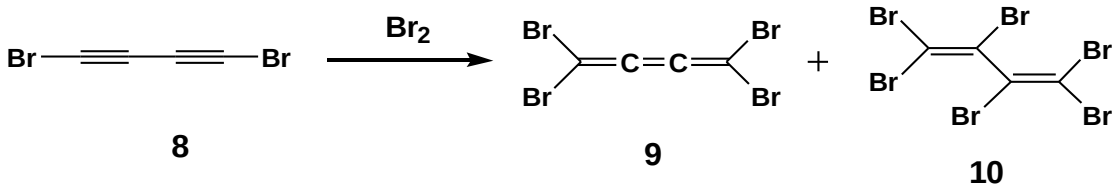
3.2.1 Synthesis of Monomer 8

Dibromobutadiyne **8** was prepared by a similar method for diiodobutadiyne, as shown in Scheme 3.1.[33]



Scheme 3.1 Synthesis of monomer **8**.[32]

The reaction started at 0 °C to avoid the possible explosion of monomer. However after 2 days, the starting material is still unreacted. Another reaction was run at room temperature with only 20 mg starting material for safety concern. After worked up, a white flake solid was observed but it quickly melted and exerted characteristic odors which is consistent with previous report.[34] However, these are not enough to prove the presence of dibromobutadiyne. NMR characterization of the monomer is unsuccessful. Room temperature NMR analysis showed nothing and Raman spectrum only showed high fluorescent background.



Scheme 3.2 Single and double bromination of dibromobutadiyne[32]

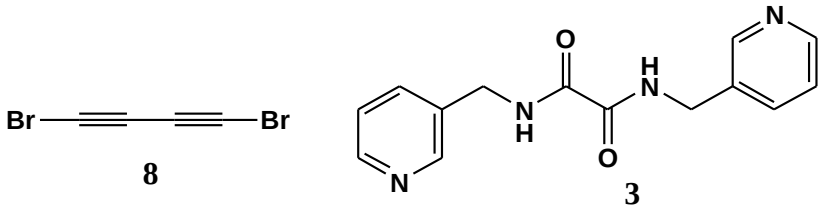
Since the characterization of monomer is difficult, using the monomer as a reagent to form a stable compound is a better approach. If we were able to characterize the stable compound, it could also prove the existence of dibromobutadiyne as a intermediate. Previous group member Pei-Hua Liu and coworkers reported the single and double bromination of dibromobutadiyne.[33] (Scheme 3.2)

Compound **10** is a much more stable compound which could be stored at room temperature for a long time. Therefore the same reaction was repeated and **10** was synthesized successfully as a major compound. The presence of dibromobutadiyne was confirmed and the experiment of growing cocrystals was continued.

3.2.2 Experiment to form cocrystals between 8 and 3

Hosts **3**, **5**, **6** and **7** were selected in the experiment. Among these hosts, compound **3**, which has pyridyl groups, could provide a stronger halogen bond. Although monomer is not stable, it is hypothesized that halogen bonding to hosts could separate monomer **8** from nearby ones and avoid random polymerizations. Started with host **3**, a series of experiments for growing cocrystal **8·3** were tried. (Table 3.1)

Table 3.1 Cocrystallization of **8·3** at room temperature and ice bath



Solvents	Temperature	Result
Methanol	Room Temperature	Yellow oil & White Solid*
Acetonitrile	Room Temperature	Yellow oil & White Solid*
CH2Cl2	Room Temperature	Yellow oil & White Solid*
THF	Room Temperature	Yellow oil & White Solid*
Methanol	Ice Bath (0°C)	Yellow oil & White Solid*
Acetonitrile	Ice Bath (0°C)	Yellow oil & White Solid*
CH2Cl2	Ice Bath (0°C)	Yellow oil & White Solid*
THF	Ice Bath (0°C)	Yellow oil & White Solid*

*Host (15mg) and guest (40 mg) were dissolved in 3 mL solvent which evaporates for one and a half days. Two different phases were observed – yellow oil and white solid. The melting point of white solid is identical with the one of host. It is suspected dibromobutadiyne decomposed into yellow oil and unreacted host remained white solid.

Hosts were dissolved in methanol, acetonitrile, dichloromethane and THF separately. Each host solution was mixed with excessive amount of guest - more than 2 equivalents and transferred into crystallization dishes. The crystallization experiment was performed at room temperature. It took 1-2 days to evaporate all

the solvents. Yellow oil and white solid were obtained separately in all the crystal dishes. Melting point of each solid was tested. Compared to host **3** and guest **8**, each white solid contained the decomposed monomer and unreacted host. Cocrystallization experiment was not successful.

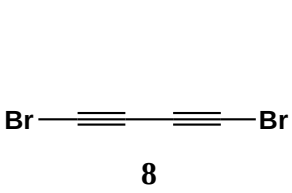
It is suspected that monomer **8** decomposed quickly so that host **3** did not have enough time to form cocrystal with it. To slow the decomposition of monomer, the temperature was decreased. Another set of experiments were tried in ice bath. Nonetheless, yellow oil and white solid were observed again. Temperature should be decreased even more to stabilize monomer **8**.

A VWR refrigerated circulator cooling bath, which could lower temperature down to -30 °C using ethylene glycol and water mixture, was purchased to decrease the cocrystallization experiment. Using the cooling bath, another series of crystallization experiments were performed at -8°C. (Table. 3.2)

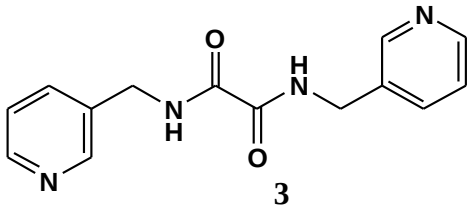
In previous attempts of forming cocrystals at room temperature or in ice bath, the monomer **8** quickly decomposed, leaving yellow oil mixed with white solid in crystal dishes. However, in the third trial at -8°C the monomer **8** did not quickly decompose. Two separate white phases were found in the crystal dish. One phase is host and the other is dibromobutadiyne. Warming the crystal above 0°C, dibromobutadiyne quickly melted and decomposed, leaving yellow oil. It means

dibromobutadiyne is significantly more stable at -8 °C than at 0 °C. Although the experiments were not successful, the monomer was stabilized. (Table. 3.2)

Table 3.2 Cocrystallization of **8·3** at -8 °C



8



3

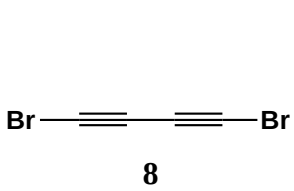
Solvents	**Temperature**	**Result**
Methanol	-8 °C	2 White Solid Phase*
Acetonitrile	-8 °C	2 White Solid Phase*
CH_2Cl_2	-8 °C	2 White Solid Phase*
THF	-8 °C	2 White Solid Phase*
Toluene	-8 °C	2 White Solid Phase*
$CHCl_3$	-8 °C	2 White Solid Phase*

*Host (15mg) and guest (40 mg) were dissolved in 3 mL solvent which evaporates for 2 days. Two different white solid phases were observed. The melting point of one phase of white solid is identical with the one of host. The other white solid phased decomposed to yellow oild upon warming to 0 °C.

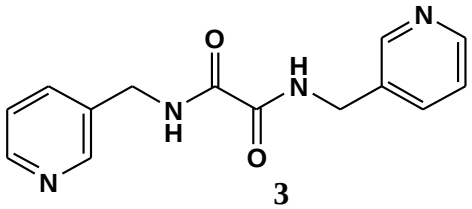
Later the temperature was decreased to -15 °C. At -15 °C, the solubility of host changes. In solvents including THF, acetone, ethanol and toluene, host could be

solubilized with similar amount of solvents at -15 °C comparing to room temperature. In dichloromethane, the solubility of host **3** decreases significantly at -15 °C. A few drops of methanol were added to the 3 mL mixture solutions increase solubility of host **3**. The mixture turned from cloudy to clear within seconds. Below are the cocrystallization trials. (Table. 3.3)

Table 3.3 Cocrystallization of **8·3** at -15 °C



8



3

Solvents	Temperature	Result
CH_2Cl_2 and MeOH	-15 °C	Blue solid.
Acetone	-15 °C	2 White Solid Phase*
Ethanol	-15 °C	2 White Solid Phase*
Toluene	-15 °C	2 White Solid Phase*
THF	-15 °C	2 White Solid Phase*
CH_2Cl_2	-15 °C	2 White Solid Phase*
MeOH	-15 °C	2 White Solid Phase*

*Host (15mg) and guest (40 mg) were dissolved in 3 mL solvent which evaporates for 2 days. Tiny blue solid was observed in crystal dish when using dichloromethane & methanol mixture. With other solvents, two different white solid phases were observed. The melting point of one phase of white solid is identical with the one of host. The other white solid phased decomposed to yellow oil upon warming to 0 °C.

Using solvents such as acetone, ethanol, toluene, methanol and THF, host was dissolved well but not able to form cocrystal with dibromobutadiyne. With dichloromethane alone, the host precipitated out at -15 °C. However, when dichloromethane was mixed with methanol, a tiny blue solid was observed. Based on our previous experience, it is a sign of cocrystal formation.

The blue solid was analyzed. The melting point is 220 °C, much higher than the host and guest which indicates a new cocrystal was formed. Left at room temperature for 3 days to avoid any further decomposition inside the cocrystal, it turned from blue to black. Raman spectrum was taken to characterize the solid. Three peaks around 1000 cm^{-1}, 1500 cm^{-1} and 2100 cm^{-1} confirm the presence of polydiacetylene. However, the solid is not a single crystal. X-ray analysis was not successful to determine its structure.[35] (Fig **3.1**)

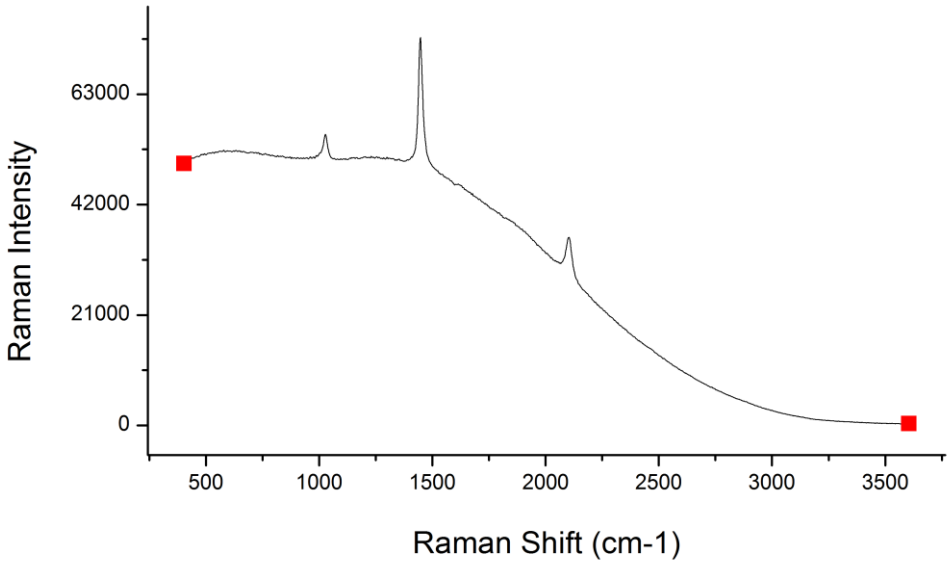


Figure 3.1 Raman spectrum of warmed blue solid[34]

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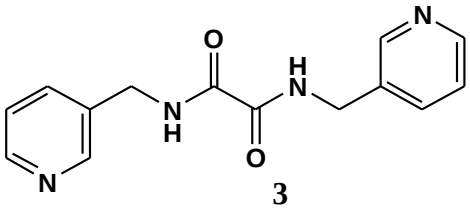
To explore why it happened in the mixed solvent, we checked the literature study of methanol and dichloromethane. It is reported that methanol and dichloromethane could form azeotrope at a 1:10 ratio.[36] The boiling point of azeotrope decreases compared to each component. Also the solubility of host increases due to the methanol portion in the azeotrope. Since the cocrystal formed in azeotrope, we did a series of solvent combinations in order to get the best result. Solvents which form azeotrope with methanol are considered. (Table. **3.4**)

Table 3.4 Azeotrope experiment I to form cocrystal **8·3** at -15°C

8



3

Solvents	Host:Guest	Results
MeOH:CH2Cl2 = 1mL : 1 mL (1:1)	25mg (H) : 37.5mg (G)	2 White Solid Phase*
MeOH:CH2Cl2 = 1mL : 2 mL (1:2)	25mg (H) : 37.5mg (G)	2 White Solid Phase*
MeOH:CH2Cl2 = 0.5mL : 2 mL (1:4)	25mg (H) : 37.5mg (G)	2 White Solid Phase*
MeOH:CH2Cl2 = 0.25mL : 2 mL (1:8)	25mg (H) : 37.5mg (G)	2 White Solid Phase*
MeOH:CH2Cl2 = 0.16mL : 2 mL (1:12)	25mg (H) : 37.5mg (G)	Blue Solid
MeOH:CH2Cl2 = 0.12mL : 2 mL (1:16)	25mg (H) : 37.5mg (G)	Blue Crystal
MeOH:CH2Cl2 = 0.1mL : 2 mL (1:20)	25mg (H) : 37.5mg (G)	Blue Crystal
MeOH:THF = 0.25mL : 2 mL (1:8)	25mg (H) : 37.5mg (G)	2 White Solid Phase*
MeOH:CHCl3 = 0.25mL : 2 mL (1:8)	25mg (H) : 37.5mg (G)	2 White Solid Phase*

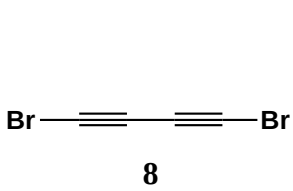
*Host (15mg) and guest (40 mg) were dissolved in 3 mL solvent which evaporates for 2 days. Blue crystal was observed in crystal dish when using dichloromethane & methanol mixture (1:12, 1:16, 1:20 ratio). With other ratio, two different white solid phases were observed. The melting point of one phase of white solid is identical with the one of host. The other white solid phased decomposed to yellow oil upon warming to 0 °C.

.

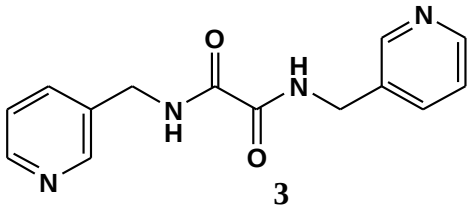
Cocrystallization worked when the ratio of methanol and dichloromethane was 1:12, 1:16 and 1:20. The azeotrope of methanol and dichloromethane played a very important role in the process. The interactions among host, guest and solvent are competitive to each other. When a strong polar solvent is used such as methanol, it forms a strong non-covalent bond to host and guest separately, interrupting the halogen bond between host and guest. With azeotrope, host could dissolve well with few amount of methanol. The halogen bond between host and guest can be preserved and dominated. The azeotrope evaporates more quickly than each solvent individually. It accelerates the process and stabilizes the guest as well. When there was too much methanol, it is hypothesized that halogen bond was interrupted and no crystal was formed. That explains when ratio of dichloromethane to methanol went below 1:8, only decomposed yellow solid was found. When there is much less methanol, the solubility of host in the solvent cannot be balanced with the guest solubility. Host precipitated out first. 1:12 methanol to dichloromethane gives the best experimental results.

We also tried other azeotrope combinations. Solvents including THF, acetonitrile, ethyl ether, toluene and chloroform were all considered. (Table 3.5)

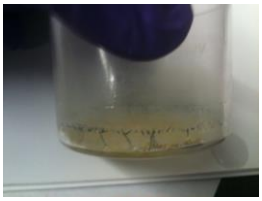
Table 3.5 Azeotrope experiment Π to form cocrystal **8·3** at -15°C



8



3

Solvents	Host:Guest	Results
MeOH:THF = 0.35mL : 2mL (1:3.3)	25mg (H) : 37.5mg (G)	
MeOH:MeCN= 1mL : 1.5 mL (1:1.4)	20mg (H) : 30mg (G)	Yellow solid
MeOH:Ethyl Ether= 1mL : 1.3 mL (1:1.3)	12mg (H) : 18mg (G)	Yellow solid
MeOH:Toluene = 0.25mL : 1.75mL (1:7)	18mg (H) : 27mg (G)	Yellow solid
MeOH:$CHCl_3$ = 0.1mL : 2 mL (1:20)	25mg (H) : 37.5mg (G)	

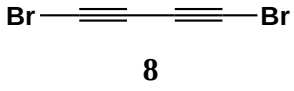
*Host and guest were dissolved in mixed solvents which evaporate in 2 days. Blue crystal was observed for the first and fifth experiment. Yellow solid was observed from the second to fourth experiment.

From those experiments, we found that some azeotrope worked for the crystallization while others did not. For the azeotrope which worked, the amount of methanol is very small, less than 0.35 mL - a tenth amount of the solution. On the other hand, the boiling point of azeotrope should be low enough to accelerate the

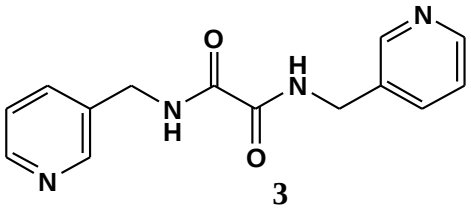
co-crystallization which explains why the methanol toluene azeotrope (Tab 3, entry 6) did not work. The azeotrope has a relatively high boiling point of 63.8 °C, which prolongs the crystallization time and induces decomposition of dibromobutadiyne prior to crystal formation.

Based on all the crystallization attempts, the dichloromethane-methanol azeotrope gave the best result. Another set of experiments were tried using different alcohols, including ethanol and isopropanol. (Tab. 3.6)

Table 3.6 Cocrystallization with different alcohol azeotrope at -15°C



8

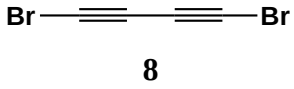


3

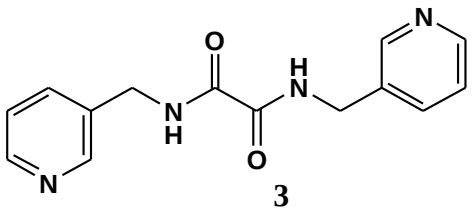
Solvents	**Host:Guest**	**Results**
EtOH:CH_2Cl_2 = 0.12 mL : 2 mL (1:16)	25mg (H) : 37.5mg (G)	Blue Crystal
EtOH:$CHCl_3$ = 0.12 mL : 2 mL (1:16)	25mg (H) : 37.5mg (G)	Blue Crystal
isopropanol: CH_2Cl_2 = 0.12 mL : 2 mL (1:16)	25mg (H) : 37.5mg (G)	Blue Crystal
iso-propanol:$CHCl_3$ = 0.12 mL : 2 mL (1:16)	25mg (H) : 37.5mg (G)	Blue Crystal
*Host and guest were dissolved in mixed solvents which evaporate in 2 days.		

Since all the successful experiments have been used halogen atom contained solvents, it was suspected that solvent with halogen atom is directly relative with cocrystallization. Another set of experiments were set up. (Table 3.7)

Table 3.7 Cocrystallization of **8** with different methanol azeotrope



8



3

Solvents	**Results**
Methanol : Acetone	Small amount of blue solid
Methanol : Ethyl Formate	Small amount of blue solid
Methanol : Iodomethane	Yellow solid
iso-propanol : CH_2Cl_2	Blue Crystal
iso-propanol : Hexane	Yellow solid

*Host and guest were dissolved in mixed solvents which evaporate in 2 days. The melting point of blue crystal is higher than host and guest. The melting point of yellow solid is identical with host.

Based on this set of experiments, ethyl formate which does not have halogen atom formed cocrystal while iodomethane did not form cocrystal. It was concluded that

cocrystallization is not fully related to halogen solvent. The combination of methanol and dichloromethane is our best choice.

After several experiments with dibromobutadiyne and 1,3-bis(pyridine)oxalamide using dichloromethane and methanol mixture, we were able to find best conditions in which cocrystal was prepared by slow evaporation of a 1:10 (methanol : dichloromethane) mixture (3 ml), containing hosts and guests (25 mg : 40 mg, 1 : 2 molar ratio) at -15°C for two days. The appearance of cocrystal **8•3** and its structure solved from X-ray diffraction is shown below.[35] (Fig. 3.2)

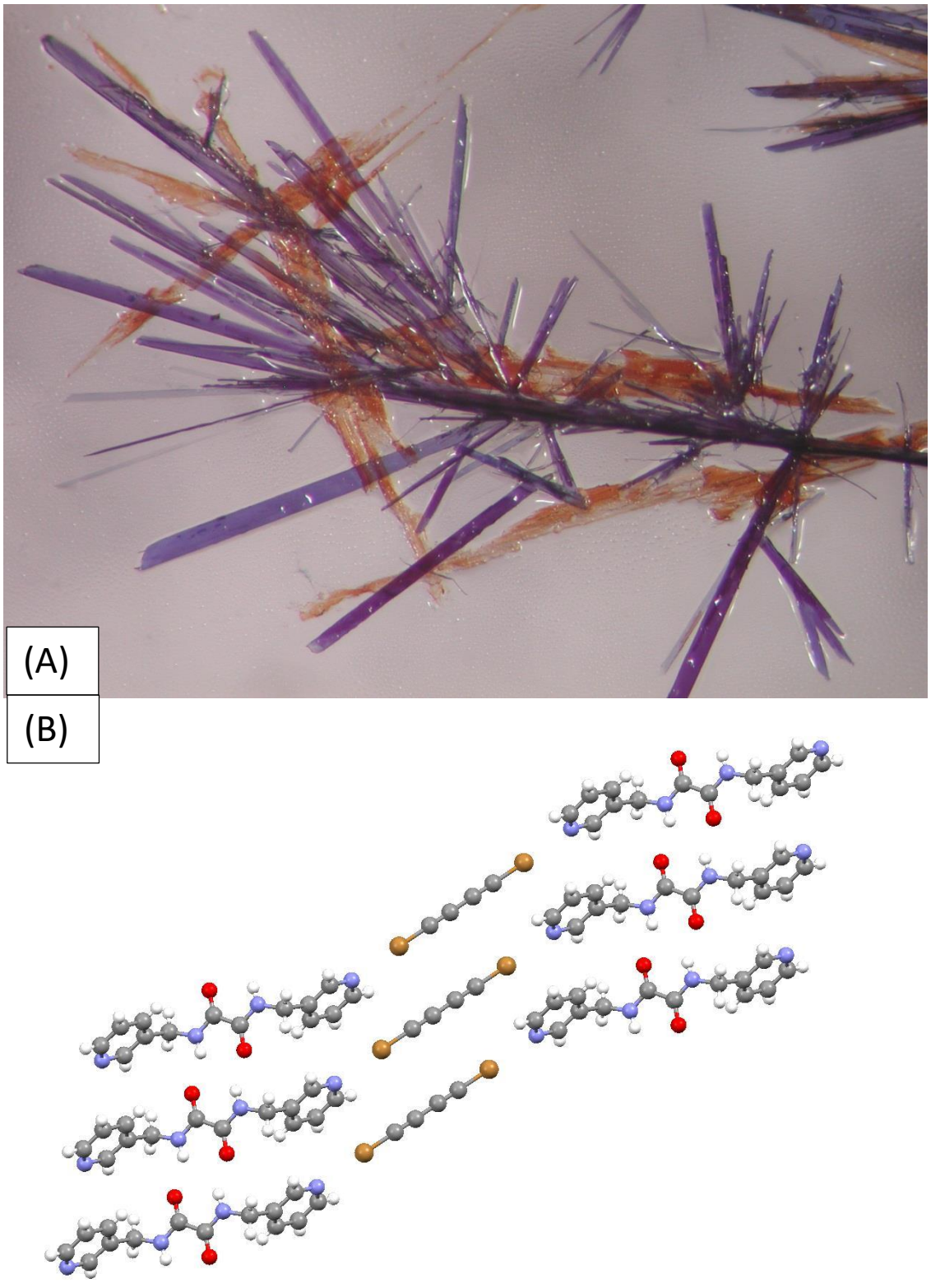


Figure 3.2 Cocrystal **3·8** A) Microscope picture of cocrystal B) X-ray structure analysis.[34] Yellow:bromine, red:oxygen, blue:nitrogen, grey:carbon, white:hydrogen

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From the X-ray analysis, we found that the monomer halogen bonded to host and was aligned in an ordered way. The repeat distance is 5.05 Å and tilt angle is 50 ° which is quite close to ideal parameter for topochemical polymerization. Therefore further research was focused on inducing polymerization of monomers.

In order to induce polymerization of monomer cocrystal, we selected 4 different crystals which had been examined as unreacted monomer cocrystals by X-ray diffraction. The first one was left at room temperature for one day. The crystal turned black. Mosaicity increased and the crystal was longer qualified for X-ray diffraction. It is hypothesized the temperature was too high. The second one was left at 4 °C refrigerator for a week. The crystal turned from clear blue to opaque dark blue. The mosaicity also increased. The third one was placed in a cooling bath at -8 °C for three days. Mosaicity increased again. The last one was placed in a cooling bath at -15 °C for over two months. The crystal did not increase mosaicity but it did not polymerize based on X-ray diffraction analysis. The polymerization of dibromobutadiyne was unsuccessful. The Raman spectrum of warmed cocrystal at room temperature was taken. It shows strong polymer peaks with high fluorescent background which indicates partial polymerization.[35] (Fig. 3.3)

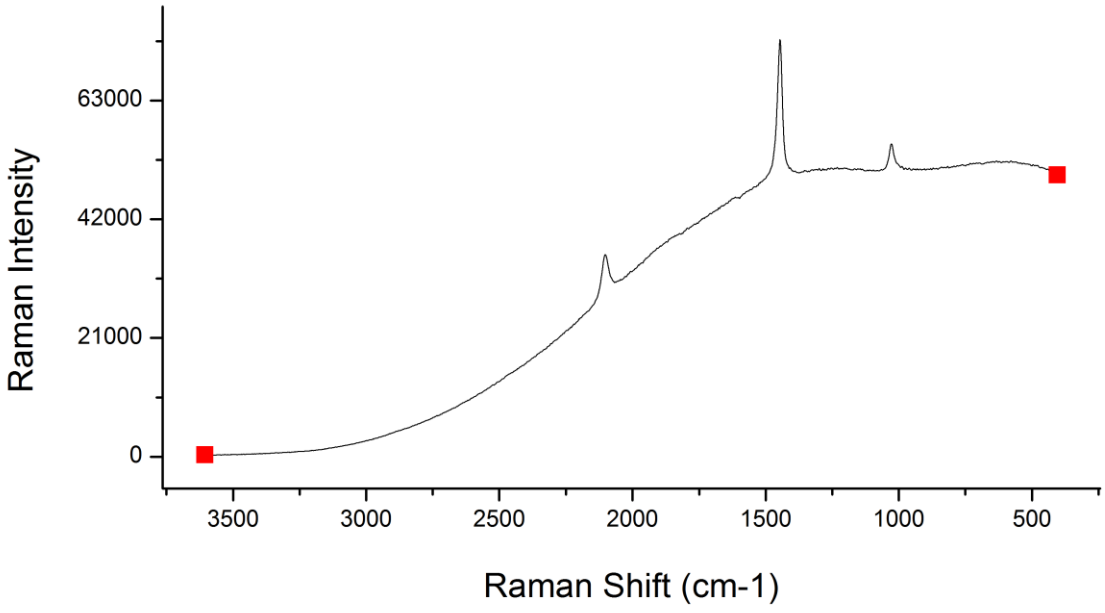

Figure 3.3 Raman spectrum of warmed partial polymerized cocrystal **3·8**[34]

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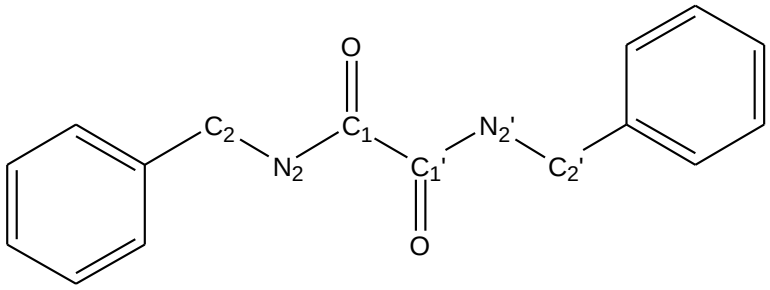


Figure 3.4 Compound **3**

Also from the successful experience of pressure induced topochemical polymerization of cocrystal **1·3**, the repeated distance decreases from 5.10 Å to

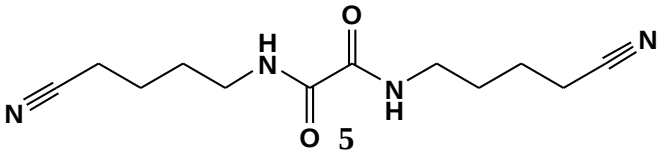
4.93 Å before and after polymerization. The title angle was 49.85 ° before polymerization. For comparison, the repeated distance of cocrystal **8·3** is 5.05 Å which is more close to the ideal parameter 4.9 – 5.0 Å and the title angle is 46 ° which is almost perfect angle. From other parameters such as angle (N2-C1-C1') – 113.4 °, angle (C2-N2-C1) – 123.7 °, they are all close to the ones of the polymer. Hence we suspect the monomer in cocrystal **8·3** could get polymerized under high pressure.

3.2.3 Experiment to form cocrystals between 8 and 5-7

Although monomer with host **3** did not give us a topochemical polymerization, it did give some experience about growing dibromobutadiyne cocrystals. Bis(nitrile)oxalamide hosts **5**, **6** and **7** were tried. In the preparation of PIDA, the bis(nitrile)oxalamide hosts, especially hosts **5** and **7**, provide the best alignment of monomer diiodobutadiyne **1** in cocrystals. However, the weaker halogen bonding between the nitrile and bromine remains a challenge. (Table 3.8, 3.9, 3.10)

Table 3.8 Cocrystallization of **8·5** at -15 °C

8

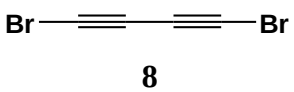


5

Solvents	**Temperature**	**Result**
CH_2Cl_2 and MeOH	-15°C	White solid*
Acetone	-15°C	White solid*
Ethanol	-15°C	White solid*
Toluene	-15°C	White solid*
THF	-15°C	White solid*
CH_2Cl_2	-15°C	White solid*
MeOH	-15°C	White solid*

*Host and guest were dissolved in mixed solvents which evaporate in 2 days. One phase of white solid was observed. The melting point of white solid is same as the one of host.

Table 3.9 Cocrystallization of **8·6** at -15°C



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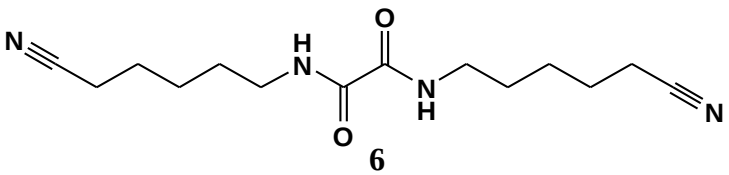
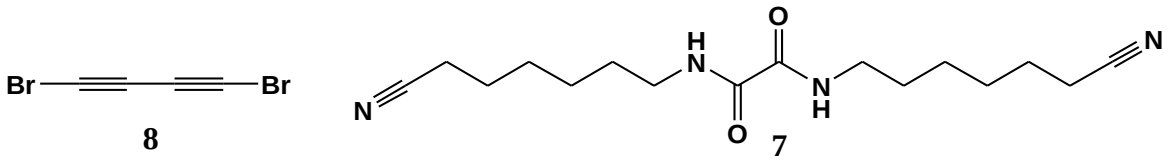


6

Solvents	**Temperature**	**Result**

CH_2Cl_2 and MeOH	-15°C	Blue crystal
Acetone	-15°C	White solid*
Ethanol	-15°C	White solid*
Toluene	-15°C	White solid*
THF	-15°C	White solid*
CH_2Cl_2	-15°C	Blue crystal
MeOH	-15°C	White solid*
*Host and guest were dissolved in mixed solvents which evaporate in 2 days. The melting point of blue crystal is higher than host and guest. The melting point of white solid is same as the one of host.		

Table 3.10 Cocrystallization of **8·7** at -15 °C



Solvents	Temperature	Result
CH_2Cl_2 and MeOH	-15°C	White solid
Acetone	-15°C	White solid
Ethanol	-15°C	White solid
Toluene	-15°C	White solid
THF	-15°C	White solid
CH_2Cl_2	-15°C	White solid
MeOH	-15°C	White solid

*Host and guest were dissolved in mixed solvents which evaporate in 2 days. One phase of white solid was observed. The melting point of white solid is same as the one of host.

Diyne **8** was mixed with hosts **5**, **6** and **7** separately using a variety of solvents including THF, dichloromethane, methanol, chloroform, acetonitrile, acetone, toluene and ethyl acetate. With host **5**, crystal was not observed. Host and guest precipitated separately no matter which solvent was used. Monomer decomposed afterwards. With host **7**, host and guest also precipitated on their own, resulting

white solids. With host **6**, monomer and host formed deep blue cocrystals in dichloromethane at -18 °C. Rinsing it with pentane to remove excess amount of monomer from the surface and slow warming to 20°C, the diyne topochemically polymerized, leading to a change in color from purple blue to a coppery, metallic appearance.(Fig. 3.5) However, these crystals are polycrystalline, single X-ray diffraction was not successful.

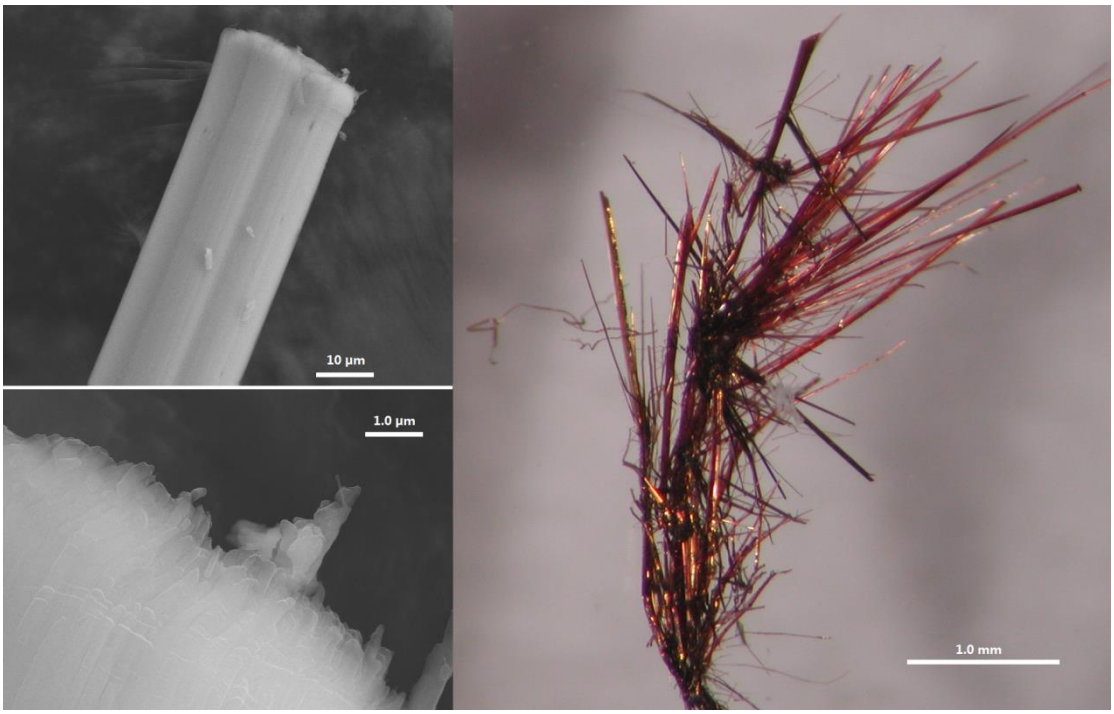


Figure 3.5 SEM image and microscope image of cocrystal **6·8**[34]

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The Raman spectroscopy indicates the abundant presence of the polymer. The strong peaks at 1030 cm^{-1}, 1441 cm^{-1}, and 2104 cm^{-1} are all consistent with the peaks of polymer. Compared with partially polymerized monomer, cocrystal **6·8** has much stronger intensity and very low fluorescent background.[35] (Fig. 3.6)

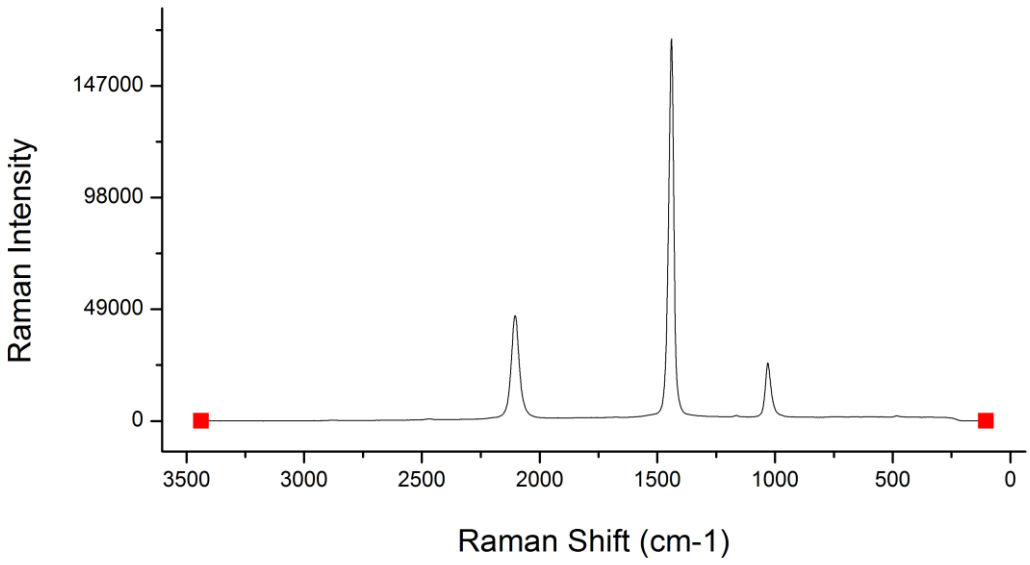

Figure 3.6 Raman spectrum of cocrystal **6·8** after warmed[34]

Although Raman spectrum indicated the high polymerization degree on the crystal surface, whether polymerization took place throughout the cocrystal is not unknown. The cocrystal was not single-crystal therefore X-ray diffraction was not accessible. With the help of Brian Philips , we were able to obtain solid-state NMR spectrum of cocrystal. To better understand the polymerization of dibromobutadiyne, we also obtained solid state NMR spectrum of partial

polymerized cocrystal **3·8**, unpolymerized **6·8** at -40 °C and polymerized **6·8** at room temperature for comparison.[35] (Fig. 3.7)

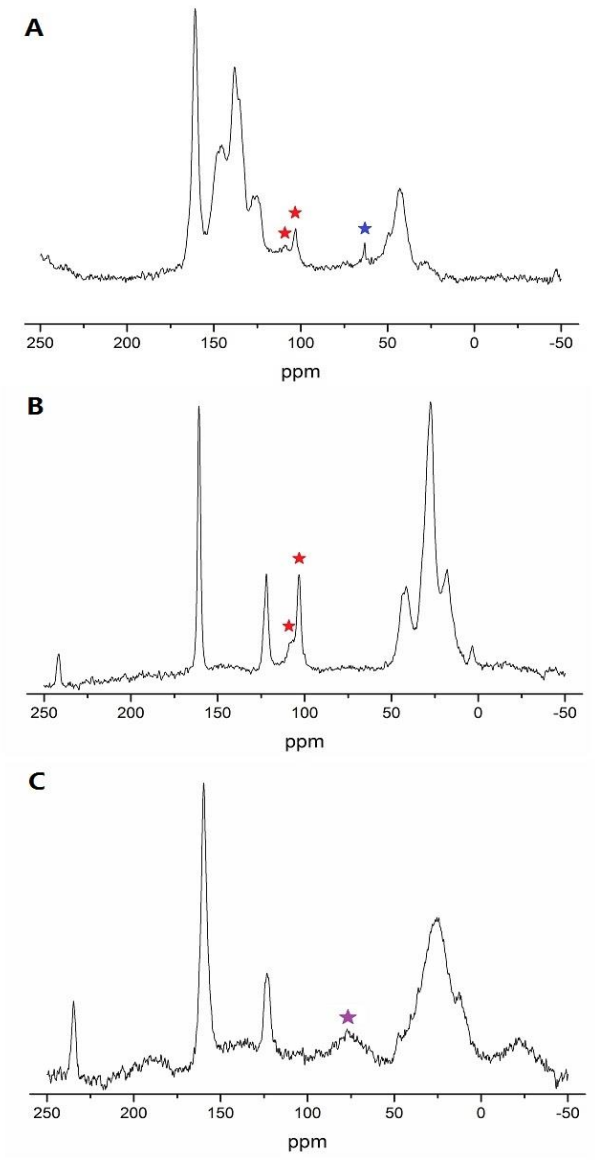

Figure 3.7 Solid state NMR A) partial polymerized cocrystal **3·8** B) unpolymerized **6·8** at -40 °C C) polymerized **6·8** at room temperature[34]

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From the solid-state NMR spectrum of those three samples, (Fig 3.6) it was confirmed that the copper-colored cocrystals contained full polymerized PBDA. The solid-state NMR of cocrystal **6•8** which was warmed to room temperature (Fig 3.6B) showed only two peaks apart from peaks for host **5** - a sharp peak at 103 ppm and a broader peak at 108 ppm which overlaps with the sharp peak. These two peaks do not match monomer **8**, which has two NMR peaks at 66.7 and 39.0 ppm in solution reported by Dembinski and coworkers.[37] Comparing to the NMR range of PIDA and other similar halogen alkene, the chemical shifts 103 ppm and 108 ppm do locate in a similar range. The breadth of the peak at 108 ppm is consistent with a carbon bonded to bromine, The strong quadrupolar interaction between bromine and the α-carbon broaden the peak at 108 ppm.

^{13}C NMR of partially polymerized cocrystal **3•8** provided important information.(Fig 3.6A) It contained the polymer peaks at 108 and 103 ppm, also the monomer peak 66.7 was observed. The other monomer peak 39.0 ppm was overlapped by the host peaks.

Comparing the polymer peaks in cocrystal **3•8** to **6•8**, the cocrystal **6•8** has much stronger intensity, revealing a clean and fully topochemical polymerization on cocrystal **6•8**. (Fig 3.7A) Meanwhile, low temperature solid-state ^{13}C CP-MAS NMR on co-crystal **6•8** showed different peaks.(Fig 3.7B) Judged by color change from purple blue to partially copper when cocrystal was kept in freezer, it was

believed monomer in cocrystal **6•8** was still very active and already underwent partially polymerization or oligmerization reaction. Cocrystal was inhomogeneous distributed and broad mixed peaks in a range of 64-84 ppm were observed, including monomer peak at 66.9 ppm. The α-carbon peak of the monomer at 39.0 ppm is hidden by the methylene group of the host. Polymer peaks at 103 and 108 ppm are absent.[35] (Fig 3.7C)

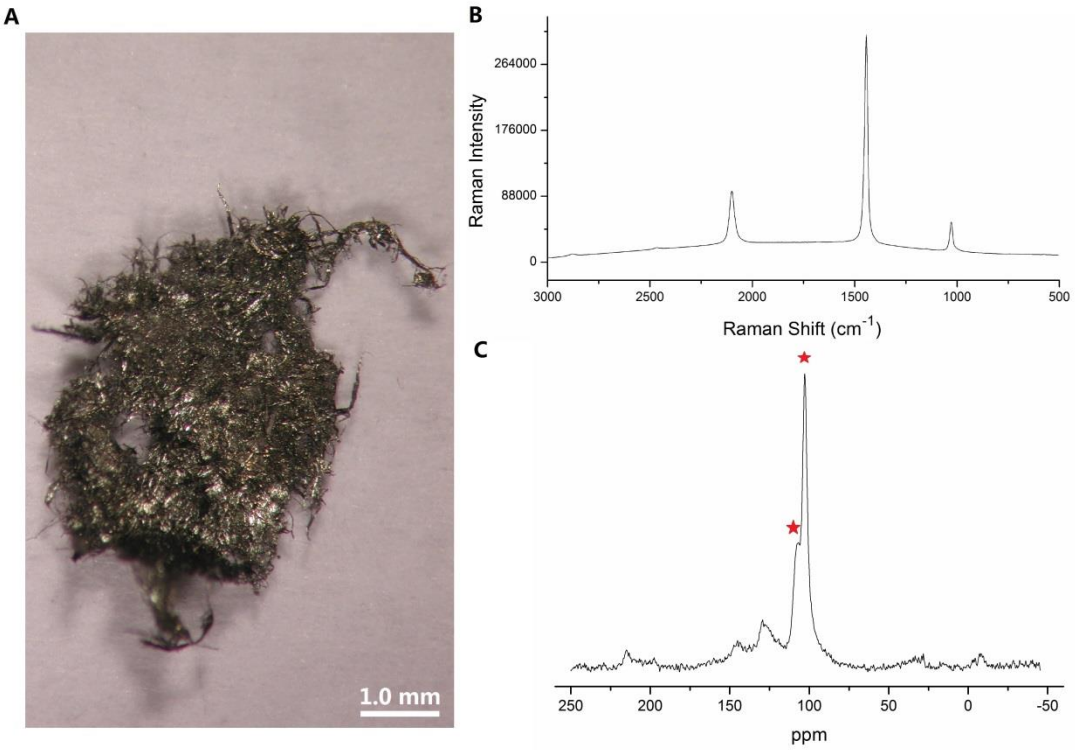
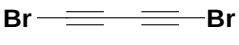


Figure 3.8 Microscope, Raman spectrum and Solid-state NMR. (A) Morphology of the isolated PBDA; (B) Raman spectrum of the isolated PBDA; (C) solid-state ^{13}C direct-excitation MAS NMR spectrum of isolated PBDA. Red stars present polymer peaks.[34]

After the preparation of PBDA•**6** cocrystal, we were trying to isolate PBDA. A series of solvents were tried including methanol, acetone, dichloromethane and THF. The procedure was to dissolve the cocrystal with solvent, sonicate 15 minutes and centrifuge 20 minutes at 1000 rpm to separate solution and solid. Repeating the same procedure 3 times, isolated PBDA was obtained at a high yield. Among those solvents, dichloromethane gave the best result. A shinny greenish material is obtained. (Fig 3.8A) Raman spectrum and solid state NMR were taken. Compared with the Raman spectrum of PBDA•**8** (Fig 3.8B), the similar stronger intensity Raman spectrum (Fig 3.8B) also indicates the abundant existence of PBDA. Also from Solid-state NMR, the dominant peaks at 103 and 108 ppm which fit perfectly with the ones in polymer demonstrate the successful isolation of PBDA polymer. (Fig 3.8C) More importantly, we are excited to find that the isolation of PBDA does not accompany with the dehalogenation of PBDA. This is the only first time that we are able to prepare and isolate a simplest Polydiacetylene.

3.3 Experimental

Safety note: Dibromobutadiyne (2) is explosive at room temperature. To reduce risks of explosion, compound 2 was prepared only in quantities of less than 200 mg. Dibromobutadiyne should be used immediately, or kept in solution at ≤ 0°C or as a solid at ≤ -40°C. When it was prepared, it was immediately mixed with host solutions, pipetted into an evaporating dish cooled to -78 °C and transferred to the chiller.



8

Dibromobutadiyne 8: Bis(trimethylsilyl)butadiyne (50 mg, 0.257 mmol) was dissolved in 200 mL acetone in a round-bottom flask which was wrapped with aluminum foil. AgNO3 (87.3 mg, 0.514 mmol) and NBS (92.57 mg, 0.514 mmol) was added and the mixture was stirred at dark for 4 hours. Solvent was removed in ice bath. A short plug (SiO_2/Cold Pentane) was used to afford a colorless solution 30 mL. To stabilize 8, pentane was not *vacuo* removed. The solution of 8 was kept in refrigerator for immediate use.

Table 3.1, Entry 1: host **3** (15 mg, 0.056 mmol) was dissolved in 3 mL methanol. The solution was subjected to sonication for 1 minute and was transferred to a 10 mL small vial. 30 mL solvent of guest **8** in a round-bottom flask was *vacuo* removed in ice bath. After pentane was removed, the host solution was added into the round-bottom flask which was swirled quickly. The mixed solution was decanted into a crystallization dish. The dish was covered with aluminum foil

which was punctured 9 holes by needles. The dish was left on the benchtop for 1-2 days until the solvent evaporates off.

Table 3.1, Entry 2-4: The procedures were the same as Entry 1. The only difference is the solvent used to dissolve host. Acetonitrile was used in Entry 2. Dichloromethane was used in Entry 3. THF was used in Entry 4.

Table 3.1, Entry 5: host **3** (15 mg, 0.056 mmol) was dissolved in 3 mL methanol. The solution was subjected to sonication for 1 minute and was transferred to a 10 mL small vial. The vial was placed in refrigerator ready for use. 30 mL solvent of guest **8** in a round-bottom flask was *vacuo* removed in ice bath. After pentane was removed, the host solution was added into a round-bottom flask which was swirled quickly. The mixed solution was decanted into a crystallization dish. The dish was covered with aluminum foil which was punctured 9 holes by needle. The dish was left in ice bath for 1-2 days until the solvent evaporated off.

Table 3.1, Entry 6-8: The procedure was the same as Entry 5. The only difference is the solvent used to dissolve host. Acetonitrile was used in Entry 6. Dichloromethane was used in Entry 7. THF was used in Entry 8.

Table 3.2, Entry 1: host **3** (15 mg, 0.056 mmol) was dissolved in 3 mL methanol. The solution was subjected to sonication for 1 minute and was transferred to a 10 mL small vial. The vial was placed in refrigerator ready for use. 30 mL solvent of guest **8** in a round-bottom flask was *vacuo* removed in ice bath. After pentane was removed, the host solution was added into a round-bottom flask which was swirled quickly. The mixed solution was decanted into a crystallization dish. The dish was covered with aluminum foil which was punctured 9 holes by needle. The dish was left in the cooling bath, in which temperature was -8 °C, for 1-2 days until the solvent evaporated off.

Table 3.2, Entry 2-6: The procedure was the same as Entry 1. The only difference is the solvent used to dissolve host. Acetonitrile was used in Entry 2. Dichloromethane was used in Entry 3. THF was used in Entry 4. Toluene was used in Entry 5. Chloroform was used in Entry 6.

Table 3.3, Entry 1: host **3** (15 mg, 0.056 mmol) was dissolved in 3 mL dichloromethane and 0.1 mL methanol mixture. The solution was subjected to sonication for 1 minute and was transferred to a 10 mL small vial. The vial was placed in refrigerator ready for use. 30 mL solvent of guest **8** in a round-bottom flask was *vacuo* removed in ice bath. After pentane was removed, the host solution was added into the round-bottom flask which was swirled quickly. The mixed solution was decanted into a crystallization dish. The dish was covered with aluminum foil which was punctured 9 holes by needle. The dish was left in the cooling bath, in which temperature was -15 °C, for 1-2 days until the solvent evaporated off.

Table 3.3, Entry 2-6: The procedure was the same as Entry 1. The only difference is the solvent used to dissolve hosts. Acetonitrile was used in Entry 2. Ethanol was used in Entry 3. Toluene was used in Entry 4. THF was used in Entry 5. Methanol was used in Entry 6.

Table 3.4, Entry 1: host **3** (15 mg, 0.056 mmol) was dissolved in 1 mL dichloromethane and 1 mL methanol mixture. The solution was subjected to sonication for 1 minute and was transferred to a 10 mL small vial. The vial was placed in refrigerator ready for use. Solvent of guest **8** in a round-bottom flask was *vacuo* removed in ice bath. After pentane was removed, the host solution was added into the round-bottom flask which was swirled quickly. The mixed solution was decanted into a crystallization dish. The dish was covered with aluminum foil

which was punctured 9 holes by needles. The dish was left in the cooling bath, in which temperature was -15 °C, for 1-2 days until the solvent evaporated off.

Table 3.4, Entry 2-9: The procedure was the same as Entry 1. The only difference is the solvent used to dissolve host. 1 mL methanol and 2 mL dichloromethane were used in Entry 2. 0.5 mL methanol and 2 mL dichloromethane were used in Entry 3. 0.25 mL methanol and 2 mL dichloromethane were used in Entry 4. 0.16 mL methanol and 2 mL dichloromethane were used in Entry 5. 0.12 mL methanol and 2 mL dichloromethane were used in Entry 6. 0.1 mL methanol and 2 mL dichloromethane were used in Entry 7. 0.25 mL methanol and 2 mL THF were used in Entry 8. 0.25 mL methanol and 2 mL chloroform were used in Entry 9.

Table 3.5, Entry 1: host **3** (15 mg, 0.056 mmol) was dissolved in 0.35 mL methanol and 2 mL THF mixture. The solution was subjected to sonication for 1 minute and was transferred to a 10 mL small vial. The vial was placed in refrigerator ready for use. 30 mL solvent of guest **8** in a round-bottom flask was vacuo removed in ice bath. After pentane was removed, the host solution was added into the round-bottom flask which was swirled quickly. The mixed solution was decanted into a crystallization dish. The dish was covered with aluminum foil which was punctured 9 holes by needle. The dish was left in the cooling bath, in which temperature was -15 °C, for 1-2 days until the solvent evaporated off.

Table 3.5, Entry 2-5: The procedure was the same as Entry 1. The difference is the amount of host and guest and the solvent used to dissolve host. 0.35 mL methanol and 1.5 mL acetonitrile and 25 mg host and 37.5 mg guest, which equals to 30 mL guest solution, were used in Entry 2. 1 mL methanol and 1.3 mL ethyl ether and 12 mg host and 18 mg guest, which equals to 15 mL guest solution, were used in Entry 3. 0.25 mL methanol and 1.75 mL acetonitrile and 18 mg host and 27

mg guest, which equals to 22 mL guest solution, were used in Entry 4. 0.1 mL methanol and 2 mL chloroform and 25 mg host and 37.5 mg guest, which equals to 30 mL guest solution, were used in Entry 5.

Table 3.6, Entry 1: host **3** (15 mg, 0.056 mmol) was dissolved in 0.12 mL ethanol and 2 mL dichloromethane mixture. The solution was subjected to sonication for 1 minute and was transferred to a 10 mL small vial. The vial was placed in refrigerator ready for use. 30 mL solvent of guest **8** in a round-bottom flask was *vacuo* removed in ice bath. After pentane was removed, the host solution was added into the round-bottom flask which was swirled quickly. The mixed solution was decanted into a crystallization dish. The dish was covered with aluminum foil which was punctured 9 holes by needle. The dish was left in the cooling bath, in which temperature was -15 °C, for 1-2 days until the solvent evaporated off.

Table 3.6, Entry 2-4: The procedure was proceed the same as Entry 1. The difference is the solvent used to dissolve host. 0.12 mL ethanol and 2 mL chloroform were used in Entry 2. 0.12 mL isopropanol and 2 mL dichloromethane were used in Entry 3. 0.12 mL isopropanol and 2 mL chloroform were used in Entry 4.

Table 3.7, Entry 1: host **3** (15 mg, 0.056 mmol) was dissolved in 0.2 mL methanol and 2.8 mL acetone mixture. The solution was subjected to sonication for 1 minute and was transferred to a 10 mL small vial. The vial was placed in refrigerator ready for use. 30 mL solvent of guest **8** in a round-bottom flask was *vacuo* removed in ice bath. After pentane was removed, the host solution was added into the round-bottom flask which was swirled quickly. The mixed solution was decanted into a crystallization dish. The dish was covered with aluminum foil

which was punctured 9 holes by needle. The dish was left in the cooling bath, in which temperature was -15 °C, for 1-2 days until the solvent evaporated off.

Table 3.7, Entry 2-5: The procedure was the same as Entry 1. The difference is the solvent used to dissolve host. 0.12 mL methanol and 2.8 mL ethyl formate were used in Entry 2. 0.12 mL methanol and 2.8 mL iodomethane were used in Entry 3. 0.12 mL isopropanol and 2.8 mL dichloromethane were used in Entry 4. 0.12 mL isopropanol and 2.8 mL hexane were used in Entry 5.

Table 3.8, Entry 1: host **5** (7 mg, 0.028 mmol) was dissolved in 0.2 mL methanol and 2.8 mL methanol mixture. The solution was subjected to sonication for 1 minute and was transferred to a 10 mL small vial. The vial was placed in refrigerator ready for use. 30 mL solvent of guest **8** in a round-bottom flask was *vacuo* removed in ice bath. After pentane was removed, the host solution was added into the round-bottom flask which was swirled quickly. The mixed solution was decanted into a crystallization dish. The dish was covered with aluminum foil which was punctured 9 holes by needle. The dish was left in the cooling bath, in which temperature was -15 °C, for 1-2 days until the solvent evaporated off.

Table 3.8, Entry 2-7: The procedure was the same as Entry 1. The only difference is the solvent used to dissolve host. Acetone was used in Entry 2. Ethanol was used in Entry 3. Toluene was used in Entry 4. THF was used in Entry 5. Dichloromethane was used in Entry 6. Methanol was used in Entry 7.

Table 3.9, Entry 1: host **6** (7 mg, 0.025 mmol) was dissolved in 0.2 mL methanol and 2.8 mL methanol mixture. The solution was subjected to sonication for 1 minute and was transferred to a 10 mL small vial. The vial was placed in refrigerator ready for use. 30 mL solvent of guest **8** in a round-bottom flask was *vacuo* removed in ice bath. After pentane was removed, the host solution was

added into the round-bottom flask which was swirled quickly. The mixed solution was decanted into a crystallization dish. The dish was covered with aluminum foil which was punctured 9 holes by needle. The dish was left in the cooling bath, in which temperature was -15 °C, for 1-2 days until the solvent evaporated off.

Table 3.9, Entry 2-7: The procedure was the same as Entry 1. The only difference is the solvent used to dissolve host. Acetone was used in Entry 2. Ethanol was used in Entry 3. Toluene was used in Entry 4. THF was used in Entry 5. Dichloromethane was used in Entry 6. Methanol was used in Entry 7.

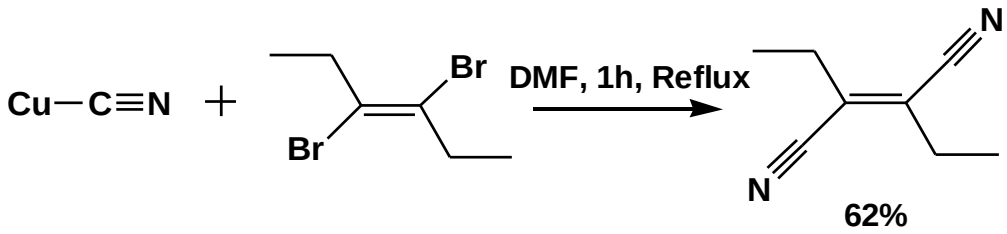
Table 3.10, Entry 1: host **7** (7 mg, 0.023 mmol) was dissolved in 0.2 mL methanol and 2.8 mL methanol mixture. The solution was subjected to sonication for 1 minute and was transferred to a 10 mL small vial. The vial was placed in refrigerator ready for use. 30 mL solvent of guest **8** in a round-bottom flask was *vacuo* removed in ice bath. After solvents pentane was removed, the host solution was added into the round-bottom flask which was swirled quickly. The mixed solution was decanted into a crystallization dish. The dish was covered with aluminum foil which was punctured 9 holes by needle. The dish was left in the cooling bath, in which temperature was -15 °C, for 1-2 days until the solvent evaporated off.

Table 3.10, Entry 2-7: The procedure was the same as Entry 1. The only difference is the solvent used to dissolve host. Acetone was used in Entry 2. Ethanol was used in Entry 3. Toluene was used in Entry 4. THF was used in Entry 5. Dichloromethane was used in Entry 6. Methanol was used in Entry 7.

Chapter 4 Post-polymerization reaction attempts on PBDA

4.1 Background

In order to functionalize polydibromodiacetylene, understanding its chemical reactivity is very important to us. However, it is very inconvenient and expensive to prepare PBDA for different experiment trials. A small molecule which has similar functional group as PBDA can simulate the chemical reactivity in PBDA and save us time and cost.



Scheme 4.1 Substitution reaction of trans-3-dibromohexene[38]

It was known that dibromoalkene is much more stable than diiodoalkene. Under Lewis basic conditions, dibromoalkene can stay stable while diiodoalkene get eliminated.[23a] It was also known that trans-3-dibromohexene could get substituted with copper(I) cyanide under reflux.[38] It suggests the stability of dibromoalkene and its derivatives is relatively higher than diiodoalkenes. By using metal catalyzed reaction, it is aimed to substitute PBDA into a variety of polydiacetylenes.

4.2 Sonogashira cross-coupling reactions on the model compounds

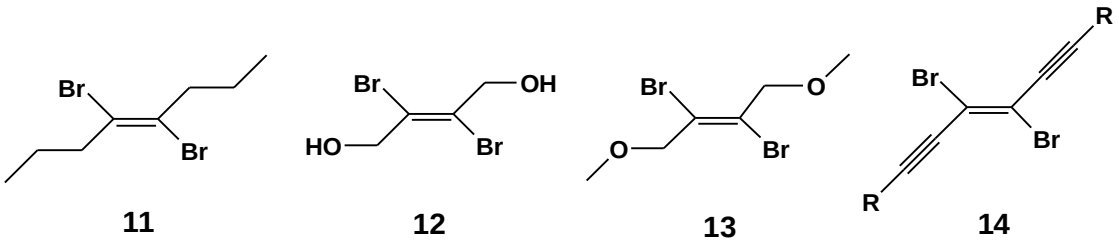
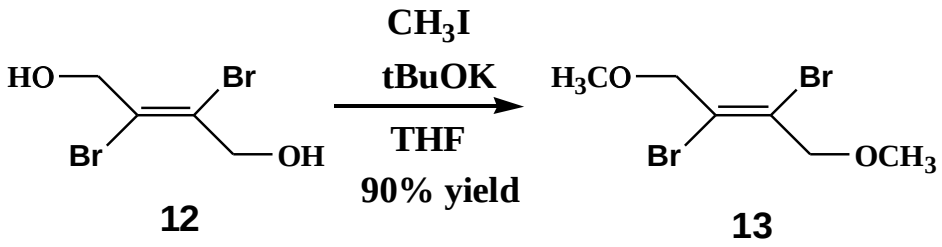


Figure 4.1 Model compounds from **11** to **14**

Compounds **11** to **14** are the model compound alternatives.(Fig. 4.1) Compound **14** contains trans-dibromoalkene and ene-yne conjugated structure which is very close to the polymer. It is a relative good compound for model reaction. However, the preparation of compound **14** is very complicated, requiring a 5-step synthesis. We turned to some simple compounds instead. Compounds **11**, **12** and **13** were selected.

Compound **11** has trans-dibromoalkene structure, and the propyl side chains which may not interfere with the chemical reactivity of the double bond. Compound **12** also has trans-dibromoalkene structure, but the alcohols will make the alkene more electron-rich, which may interfere with its chemical reactivity and the effect of acidic hydrogen is unknown. Also compound **12** are shorter which may not have steric effect, increasing its chemical reactivity. In addition, compound **12** is commercial available which give convenience for model reaction trials. Compound **13** does not have acidic hydrogen and is easy to make. It is relative the best models

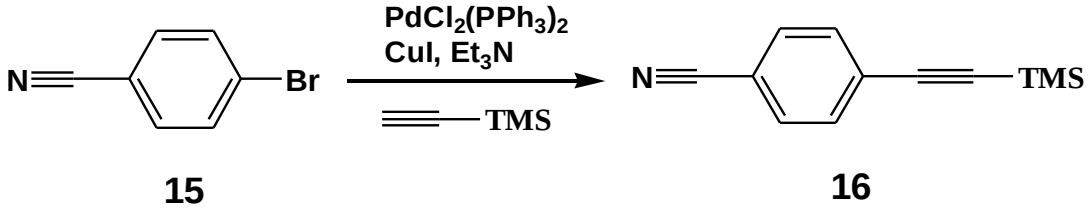
among these 3 compounds. The SN2 reaction between trans 1,4-diol-2-butene and methyl iodide gives 1,4-dimethyloxy-2-butene with 90% yield. (Scheme 4.2)



Scheme 4.2 Prepartion of compound **13**[45]

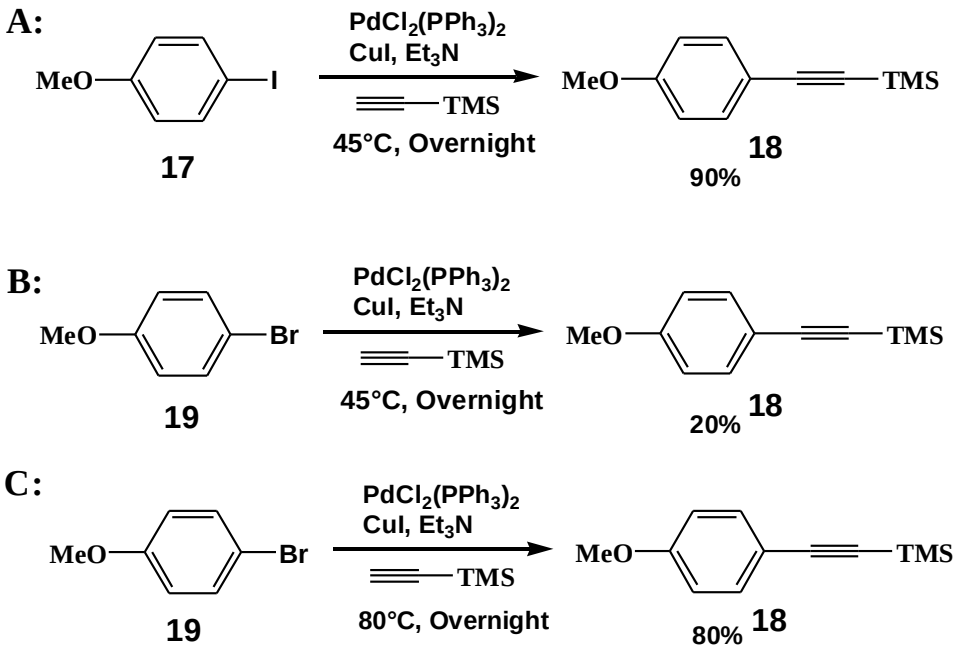
After compound **13** was prepared, Sonogashira reaction was tried initially. The Sonogashira reaction is the most commonly used cross-coupling reaction to form carbon-carbon bond between a terminal alkyne and an aryl or vinyl halide. It is hypothesized that once the polymer reacts with terminal alkynes, the solubility of the polymer could increase and push the reaction forward.

Prior to apply Sonogashira reaction on the model compound, similar Sonogashira reactions reported worked well were repeated including Xiuzhu Ang and Racquel DeCicco's work. 1-bromo-4-cyanobenzene was coupled to trimethylsilylacetylene at room temperature for overnight to afford 91% yield product. The experiment was repeated successfully to afford 85% yield product.[39] (Scheme 4.3)



Scheme 4.3 Sonogashira reaction of **15** to **16**[38]

4-methoxy-1-iodobenzene was coupled with trimethylsilylacetylene at 45 °C for overnight.[40] The difference between these two experiments is the electronic property of starting material. The cyano group is electron withdrawing and methoxy group is electron donating. Comparing these two experiments, arylbromide **15** can react at room temperature while aryliodide **17** needs to increase temperature to 45 °C for Sonogashira reaction.(Scheme 4.4) Hence the electron withdrawing functional group on the aryl or vinyl is good for sonogashira reaction. It is identical with common study about Sonogashira reaction reactivity.



Scheme 4.4 Preparation of **18** from **17** to **19**[39]

When using 4-methoxy-1-bromobenzene with trimethylsilylacetylene at 45°C, the reaction only went about 20-30% completion by NMR after 24 hours. In order to

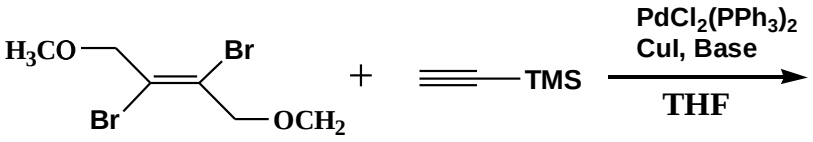
boost the reaction, reaction temperature was raised to 80 °C for 12 hours, and the reaction went about 80% completion by NMR. The iodo-compound is more active than bromo-compound in sonogashira reaction and some inert reaction could be boosted by heating. This is constant with the general understanding of Sonogashira reaction.

Based on this experience, model reactions were started. Starting 4 separated reactions at room temperature with 4 different bases including triethylamine, diisopropylamine, isopropylamine and potassium tert-butoxide, in each case the starting material remained unreacted after 24 hours. Further addition of terminal alkyne and palladium catalyst did not help. In order to push the reaction, the reaction temperature was increased to 80°C considering bromine is less reactive than iodine. With 4 different separated trials in which each base was used separately, the starting material all underwent elimination instead. 1,4-Dimethoxy-2-butyne was obtained at 90% yield.

Since starting material undergoes elimination at 80 °C, the temperature was too high for dibromoalkenes. A new set of experiments were set up. The temperature was lowered to 60 °C to avoid elimination. After 24 hours of reaction time, all the starting materials in each experiment got eliminated again, meaning the temperature was still high. The third set of experiments was tried. Temperature was set to 40 °C. After 24 hours, the starting materials remained unreacted. For all

these 4 experiments, additional two equivalent of terminal alkyne and 10% equivalent of palladium catalyst were added in each case, the starting materials remained unreacted after another 24 hours. (Table 4.1)

Table 4.1 Sonogashira reactions on model compound **13** with TMS-acetylene



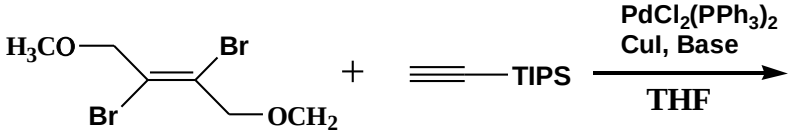
13

Base	Temperature	Result
Et_3N	20°C	No Reaction
iPr_2NH	20°C	No Reaction
n-$BuNH_2$	20°C	No Reaction
t-BuOK	20°C	No Reaction
Et_3N	80°C	1,4-Dimethoxy-2-butyne
iPr_2NH	80°C	1,4-Dimethoxy-2-butyne
n-$BuNH_2$	80°C	1,4-Dimethoxy-2-butyne
t-BuOK	80°C	1,4-Dimethoxy-2-butyne
Et_3N	60°C	1,4-Dimethoxy-2-butyne
iPr_2NH	60°C	1,4-Dimethoxy-2-butyne
n-$BuNH_2$	60°C	1,4-Dimethoxy-2-butyne

t-BuOK	60°C	1,4-Dimethoxy-2-butyne
Et_3N	40°C	No reaction
IPr_2NH	40°C	No reaction
n-$BuNH_2$	40°C	No reaction
t-BuOK	40°C	No reaction

To testify whether the reaction results vary with different terminal alkynes, another set of model reactions on compound **13** with (triisopropylsilyl)acetylene (TIPS-acetylene) under the same condition were tried. (Table 4.2)

Table 4.2 Sonogashira reactions on model compound **13** with TIPS-acetylene



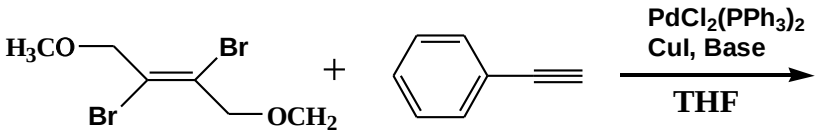
13

Base	**Temperature**	**Result**
Et_3N	20°C	No Reaction
iPr_2NH	20°C	No Reaction
n-$BuNH_2$	20°C	No Reaction
t-BuOK	20°C	No Reaction
Et_3N	80°C	1,4-Dimethoxy-2-butyne

iPr_2NH	80°C	1,4-Dimethoxy-2-butyne
n-$BuNH_2$	80°C	1,4-Dimethoxy-2-butyne
t-BuOK	80°C	1,4-Dimethoxy-2-butyne
Et_3N	60°C	1,4-Dimethoxy-2-butyne
iPr_2NH	60°C	1,4-Dimethoxy-2-butyne
n-$BuNH_2$	60°C	1,4-Dimethoxy-2-butyne
t-BuOK	60°C	1,4-Dimethoxy-2-butyne
Et_3N	40°C	No reaction
iPr_2NH	40°C	No reaction
n-$BuNH_2$	40°C	No reaction
t-BuOK	40°C	No reaction

In addition, model compound with phenylacetylene was also tried. Nevertheless, the same results were obtained. (Table 4.3)

Table 4.3 Sonogashira reactions on model compound **13** with phenylacetylene

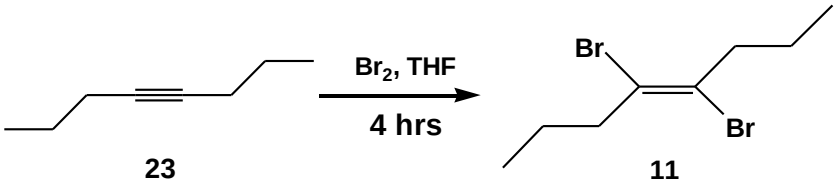


13

Base	Temperature	Result
Et_3N	20°C	No Reaction
iPr_2NH	20°C	No Reaction
n-$BuNH_2$	20°C	No Reaction
t-BuOK	20°C	No Reaction
Et_3N	80°C	1,4-Dimethoxy-2-butyne
iPr_2NH	80°C	1,4-Dimethoxy-2-butyne
n-$BuNH_2$	80°C	1,4-Dimethoxy-2-butyne
t-BuOK	80°C	1,4-Dimethoxy-2-butyne
Et_3N	60°C	1,4-Dimethoxy-2-butyne
iPr_2NH	60°C	1,4-Dimethoxy-2-butyne
n-$BuNH_2$	60°C	1,4-Dimethoxy-2-butyne
t-BuOK	60°C	1,4-Dimethoxy-2-butyne
Et_3N	40°C	No reaction
iPr_2NH	40°C	No reaction

n-$BuNH_2$	40°C	No reaction
t-BuOK	40°C	No reaction

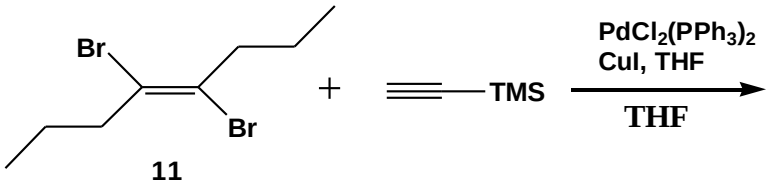
By all these trials, the Sonogashira reaction on model compound **13** was unsuccessful. Model compounds **11** and **12** underwent the same conditions.



Scheme 4.5 Preparation of model compound **11**

Using 1 equivalent of bromine reacted with 4-octyne, compound **11** was afforded with 85% yield.[41] It underwent the same Sonogashira reaction condition as the previous experiments showed.(Table 4.4)

Table 4.4 Sonogashira reactions on model compound **11** with TMS-acetylene



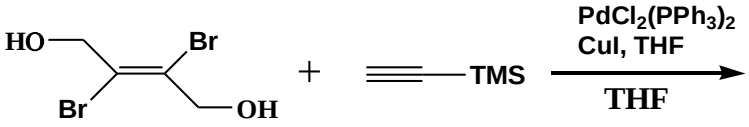
11

Base	Temperature	Result
Et_3N	20°C	No Reaction
Et_3N	80°C	4-octyne
Et_3N	60°C	4-octyne
Et_3N	40°C	No Reaction
iPr_2NH	20°C	No Reaction
iPr_2NH	80°C	4-octyne
iPr_2NH	60°C	4-octyne
iPr_2NH	40°C	No Reaction

As the above tables show, all the reactions showed similar results. When above 60°C, the model compound was eliminated. When below 40°C, the starting material remained unreacted.

The last set of model reaction was focused on compound **12**. Different with other model compounds, it has two acid hydrogens which may affect its chemical reactivity. (Table 4.5)

Table 4.5 Sonogashira reactions on model compound **12** with TMS-acetylene



12

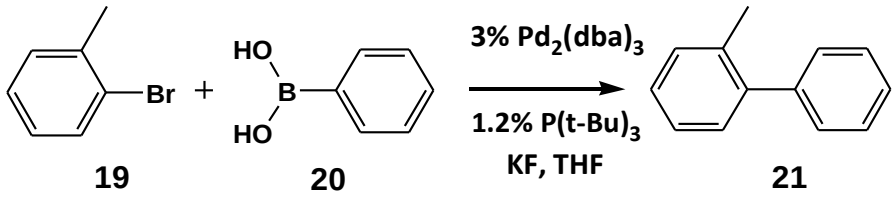
Base	Temperature	Result
Et_3N	20°C	No Reaction
Et_3N	80°C	2-Butyne-1,4-diol
Et_3N	60°C	2-Butyne-1,4-diol
Et_3N	40°C	No Reaction
iPr_2NH	20°C	No Reaction
iPr_2NH	80°C	2-Butyne-1,4-diol
iPr_2NH	60°C	2-Butyne-1,4-diol
I Pr_2NH	40°C	No Reaction

As the table shows, the model compound was eliminated above 60°C and remained unreacted below 40°C. Based on these unsuccessful model reactions, PBDA were not pursued further.

4.3 Suzuki–Miyaura cross-coupling reactions on the model compounds

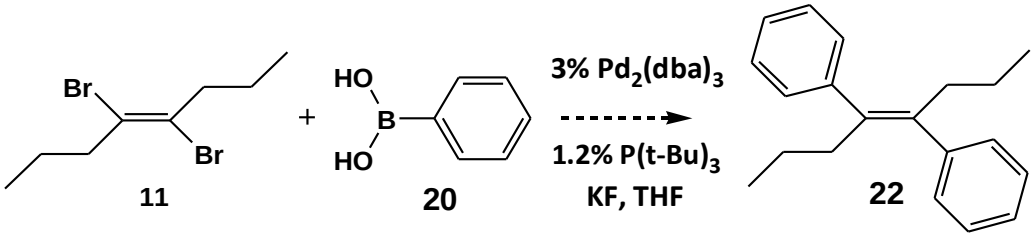
Compared to Sonogashira cross coupling reaction, Suzuki reaction usually requires relatively mild conditions which are not strictly water-sensitive. However, most of the Suzuki reaction of bromine compound requires high temperature above 80°C.[41-42] We narrowed our search to very reactive catalyst system for Suzuki reaction. One reported work by Fu's group in 2000 was found in which $Pd_2(dba)_3/P(t\text{-}Bu)_3$ was used as a catalyst in Suzuki reaction at room temperature.[43] This catalyst system includes a wide range of compatible substrates including less reactive arylbromide, arylchloride, vinylbromide and vinlychloride which may be used on our model compounds. However, $P(t\text{-}Bu)_3$ is an extremely active ligand which could catch fire spontaneously if exposed to air. Hence all the reactions should be conducted in the glove box. Thanks to Dr. Nai's group, I could use glove box conveniently.

one of its reported reactions was repeated.(Scheme 4.6) The repeated experiment affords 93% yield which is same as reported work. Model compounds were tried with the same condition for Suzuki coupling reaction.[43]



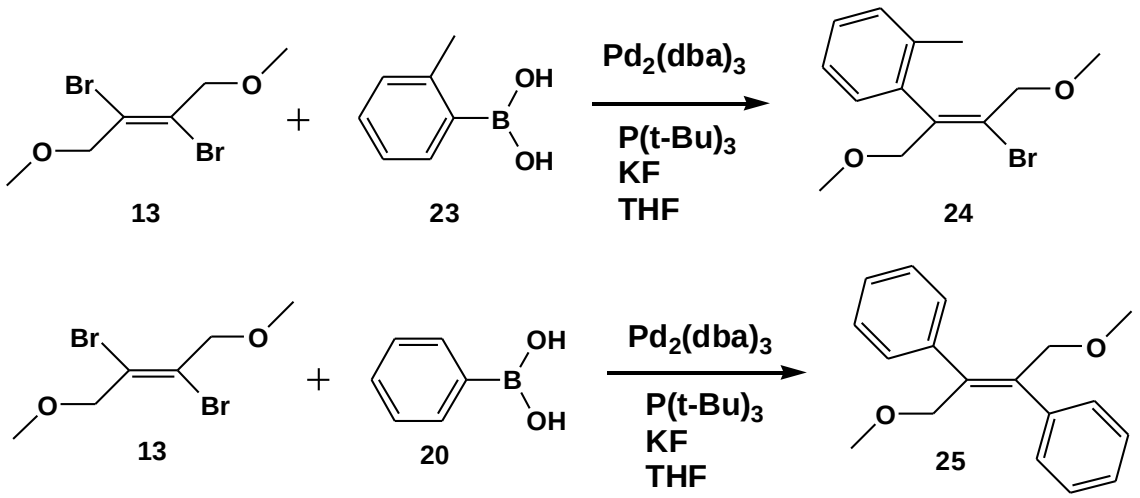
Scheme 4.6 $Pd_2(dba)_3/P(t\text{-}Bu)_3$ catalyzed Suzuki reaction[41]

However, the reaction was not successful. According to ^{13}C NMR, a great percentage of starting material remained unreacted and a small percentage of mono-substituted alkene was obtained.(Scheme 4.7) The desired di-substituted alkene was not observed. A small percent of one side substitution was observed, making it very hard to apply onto polymer. We expected to have a model reaction worked with at least 70% yield or more.



Scheme 4.7 $Pd_2(dba)_3/P(t\text{-}Bu)_3$ catalyzed Suzuki reaction on model compound **11**

Compound **11** is not the ideal choice for model reaction. The propyl side chains may have steric effect and weaken the reactivity of dibromoalkene. Another set of experiments were tried on compound **13**.(Scheme 4.8)



Scheme 4.8 $Pd_2(dba)_3/P(t\text{-}Bu)_3$ catalyzed Suzuki reactions on model compound **13**

With *o*-tolylboronic acid, dibromoalkenes underwent mono-substituted reaction after 48 hours with less than 60% yield. With phenylboronic acid, dibromoalkenes underwent di-substituted reaction with phenylboronic acid with 72% yield after 48 hours. The reaction condition on the polymer is different with model compound. There are less steric 72% yield looks more promising to us. Suzuki reactions of phenylboronic acid with the polymer PBDA were tried afterwards.

4.4 Post-polymerization reaction attempts on the PBDA

Under the same condition, isolated PBDAs were reacted with o-tolylboronic acid and phenylboronic acid separately. After 48 hours, the reaction was worked up. By extraction of saturated NaCl solution with ethyl acetate, organic phase was separated with undissolved black solid. Mixture was centrifuged and solvent was decanted and collected. Then same amount of ethyl acetate was added again. By repeating the same procedure three times, black powder was collected and left to dry. SEM and Raman spectroscopy was used to further characterize it.

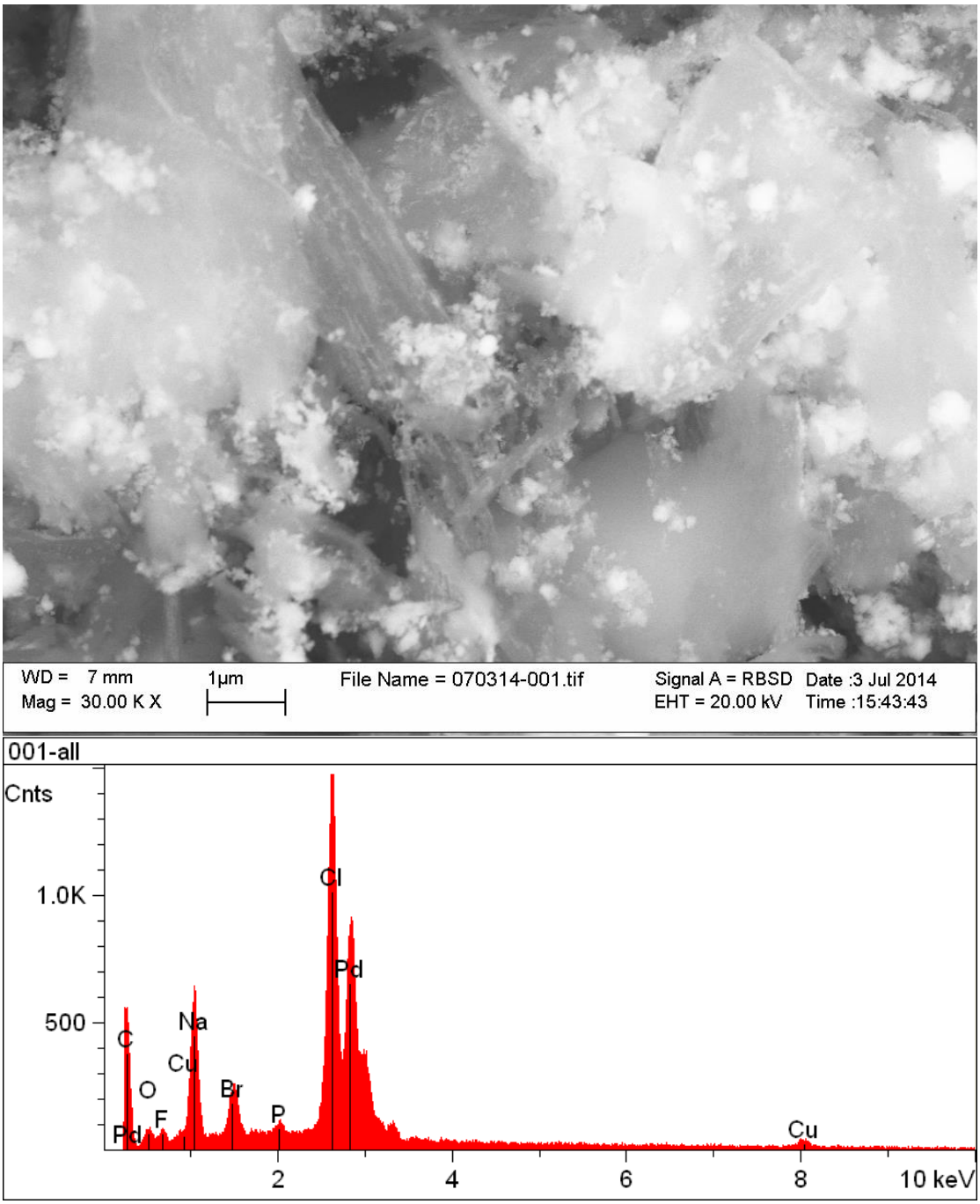


Figure 4.2 SEM and EDS spectrum analysis of black power after purifiation

From the SEM and EDS spectrum, it was seen that there were still a lot palladium complex and sodium salts leftover. The Raman spectrum did not give any valuable

information. Its intensity is too weak and there is a lot of fluorescent background. After discussing with Dr John Rudick and Dr Mingyu Nyugen and some literature research, it is found that pyridine and THF could strongly bond to palladium. Washing the mixture with THF and pyridine could remove some amount of palladium salts. Then we washed the mixture 3 times with THF and pyridine. We used 200 mL of pyridine and 200 mL of THF to wash 20 mg of isolated reacted black powder. By SEM and EDS spectrum, we observed the significant decrease amount of palladium salts, but there was still some palladium salts residue.(Fig. 4.3)

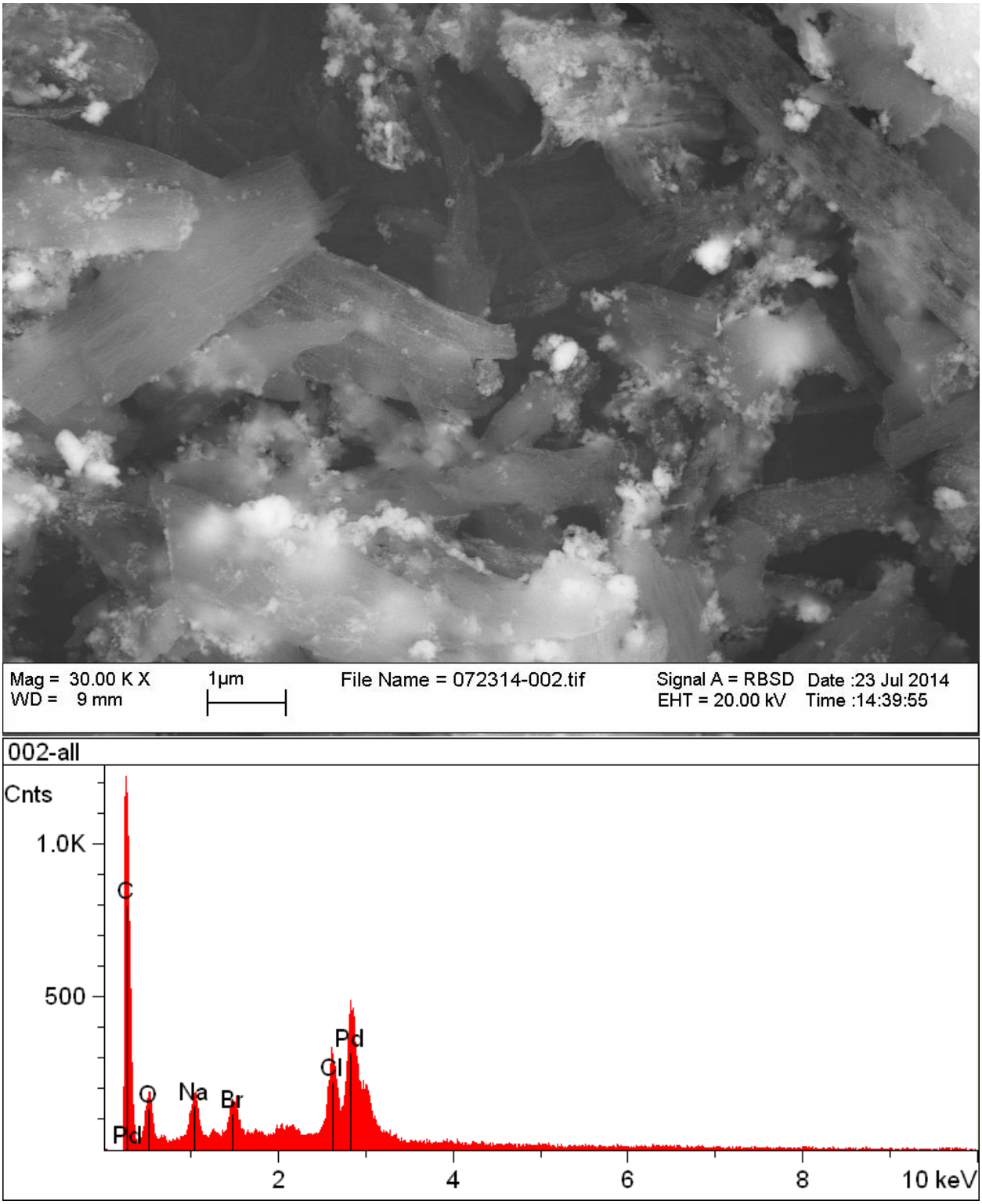
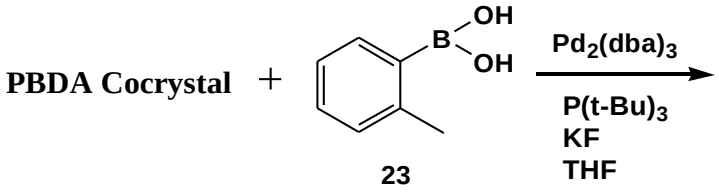


Figure 4.3 SEM and EDS spectrum analysis of black power after purifiation

The top picture shows the palladium catalyst is still around after solvent wash. The second picture indicates the amount of palladium decreases more than a half compared to previous analysis before wash. However, considering the relative peak intensity of bromine and carbon, it is estimated 100 carbon to 1 bromine which indicates a large quantity of isolated polymer was eliminated. The post-polymerization experiment was failed.

The previous trials were all based on the isolated material. That is one fact we did not consider. During the isolation of PBDA from cocrystal, the long PBDA strings would twist to each other and the inside PBDA was isolated from reactions. Reaction on the PBDA cocrystal was tried. (Scheme 4.9)



Scheme 4.9 Suzuki reaction of PBDA cocrystal and o-tolylboronic acid

Still, most of the PBDA was not reacted. SEM indicates the major presence of PBDA. Unlike before, PBDA remain unreacted after Suzuki reaction. Neither elimination nor substitution reaction were observed. The bromine and carbon peaks in EDS spectrum looks similar to unreacted PBDA.(Fig. 4.4) The Suzuki cross coupling reaction on PBDA cocrystal was unsuccessful.

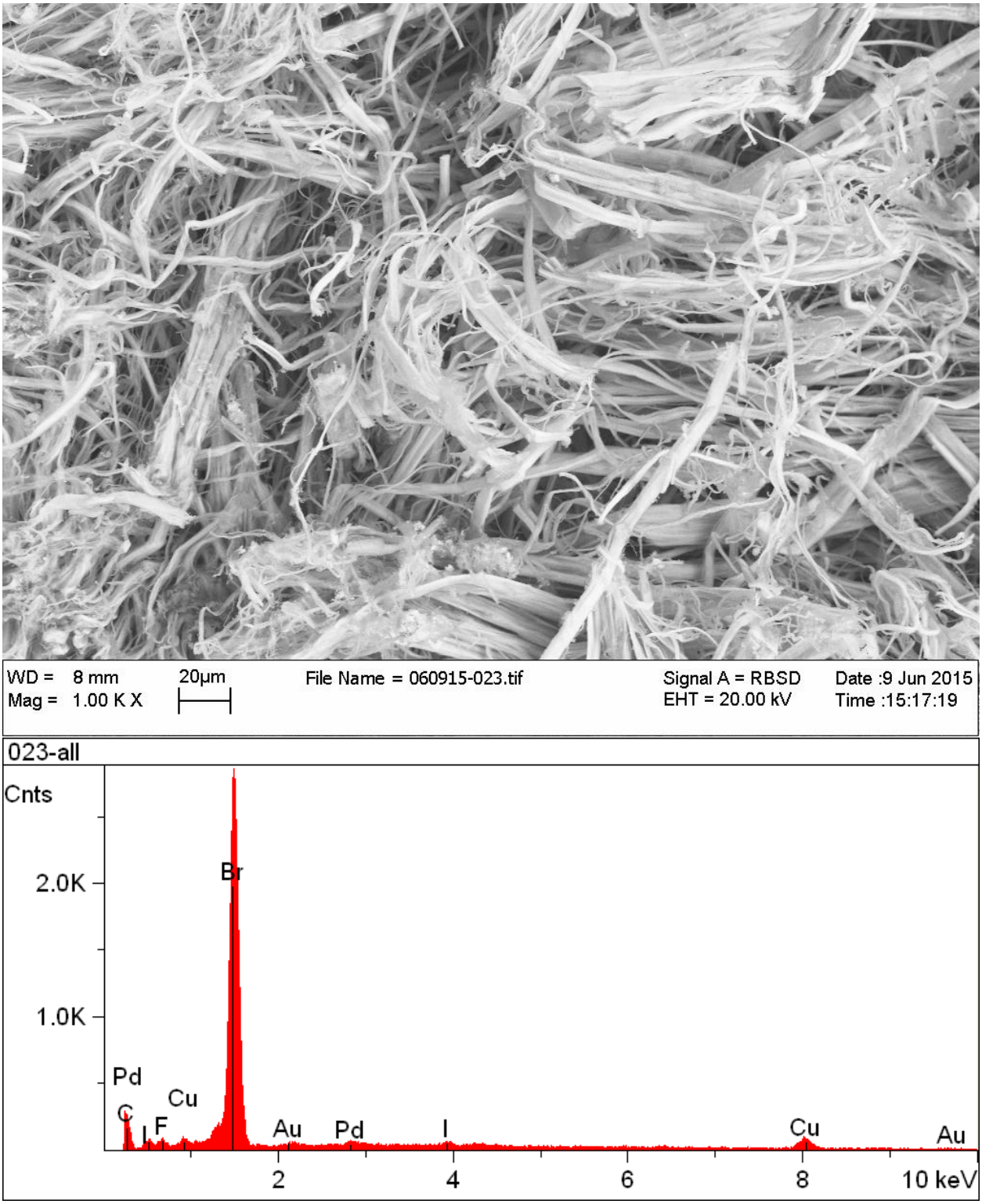
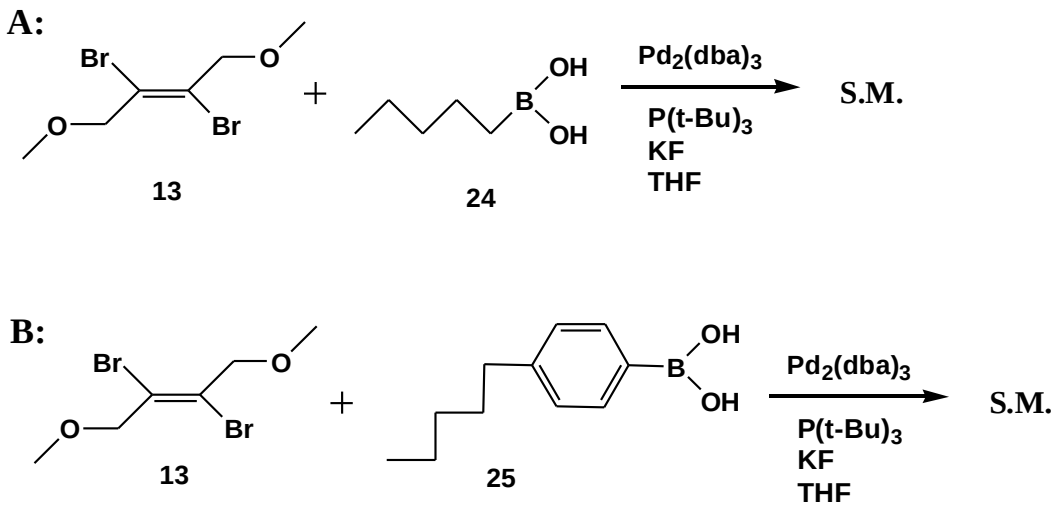


Figure 4.4 SEM and EDS spectrum of reacted PBDA cocrystal after Suzuki Reaction

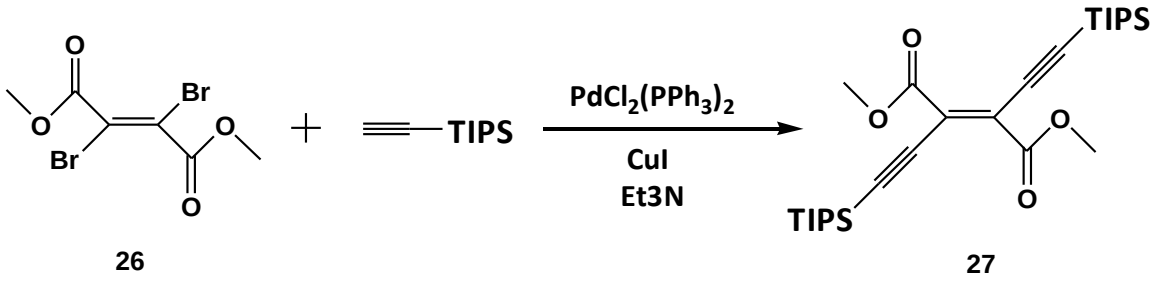
To find another way to modify PBDA, a major problem need to be addressed which is the insolubility of the PBDA. Since it is a fiber and insoluble in all the solvents, it is very difficult to characterize unless using solid-state NMR. Solid-state NMR also needs material and time – more than 20 mg and up to 7 days to characterize one sample. It is not an easy way to monitor the reaction. If the product is soluble or if the product is IR or UV or Raman active, the result of each reaction can be determined very quickly. Finding a better way to monitor the reaction is our direction for future experiment.

To solve the solubility problem, adding solubilizing groups on model compounds was tried. If similar reaction could happen, desired products can be easily separated. N-pentylboronic acid and 4-pentylphenylboronic acid were tried with dibromoalkene **13** separately. (Scheme. 4.10) For Scheme 4.10 A, starting material was still unreacted after 48 hours. For Scheme 4.10B, less than 50% of starting material reacted with 4-pentylphenylboronic acid after 48 hours. The yield is too low to allow us continue the same reaction on the polymer. Similar reaction on the polymer was not tried.



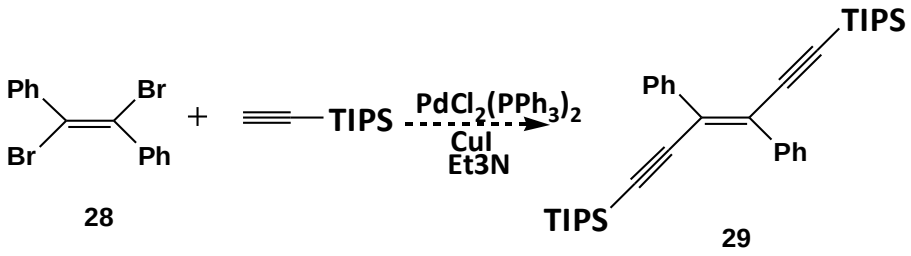
Scheme 4.10 Suzuki reaction of compound **13** with boronic acids **24** and **25**

Suzuki cross coupling reaction was failed. Sonogashira cross coupling reaction was tried again. In 1995, the Diederich group reported a series of Sonogashira reactions on dibromoalkenes. (Triisopropylsilyl)acetylene was reported successfully coupled with dibromoalkenes **26** to afford a conjugated ene-yne **27.**[44](Scheme 4.11)



Scheme 4.11 Sonogashira reaction of compound **26** with TIPS-acetylene[40]

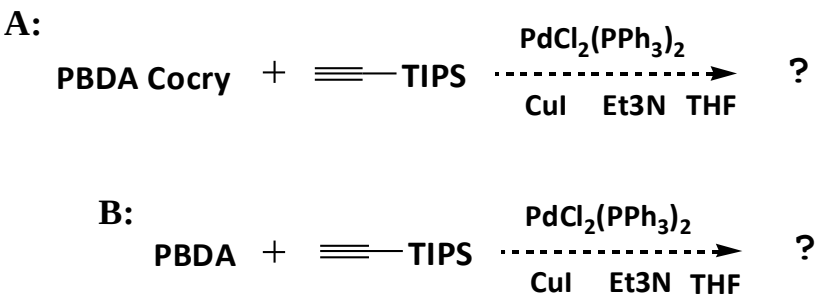
The same reaction was successfully repeated (90%). Another experiment.was tried.(Scheme 4.11) (E)-1,2-dibromo-1,2-diphenylethene did not couple with (Triisopropylsilyl)acetylene.(Scheme 4.12)



Scheme 4.12 Sonogashira reaction of compound **28** with TIPS-acetylene

Unfortunately, the reaction was unsuccessful. Starting material remained unreacted. From all those experiment, the reactivity of starting material greatly affected the experiment result. It was hard to predict the reactivity of PBDA by model compounds. PBDA was tried Sonogashira reaction.

PBDA cocrystal and isolated PBDA were separately used in separate reactions to compare the difference.(Scheme 4.12) Excessive amount of terminal alkynes were added during 12 hours reaction time. After 24-48 hours, the mixture turned black, which should result from the oxidation of palladium salts. Extraction with water filters out most of the palladium salts and centrifugation separates the homo-coupled terminal alkyne in the organic phase to give a homogenous layer of black powder.(Scheme 4.13)



Scheme 4.13 Sonogashira reaction of PBDA and PBDA cocrystal with TIPS-acetylene

By Raman spectrum and SEM, there was no strong evidence of reacted polymer. The ratio of bromine to carbon is still close to the starting material. If reaction happened, meaning TIPS-acetylenes were attached on PBDA, silicon element could be found by EDS analysis.(Fig. 4.5) However, few amount of Si was detected. The isolated PBDA and PBDA cocrystal did not show difference based on results. The Sonogashira reactions of PBDA at room temperature were not successful.

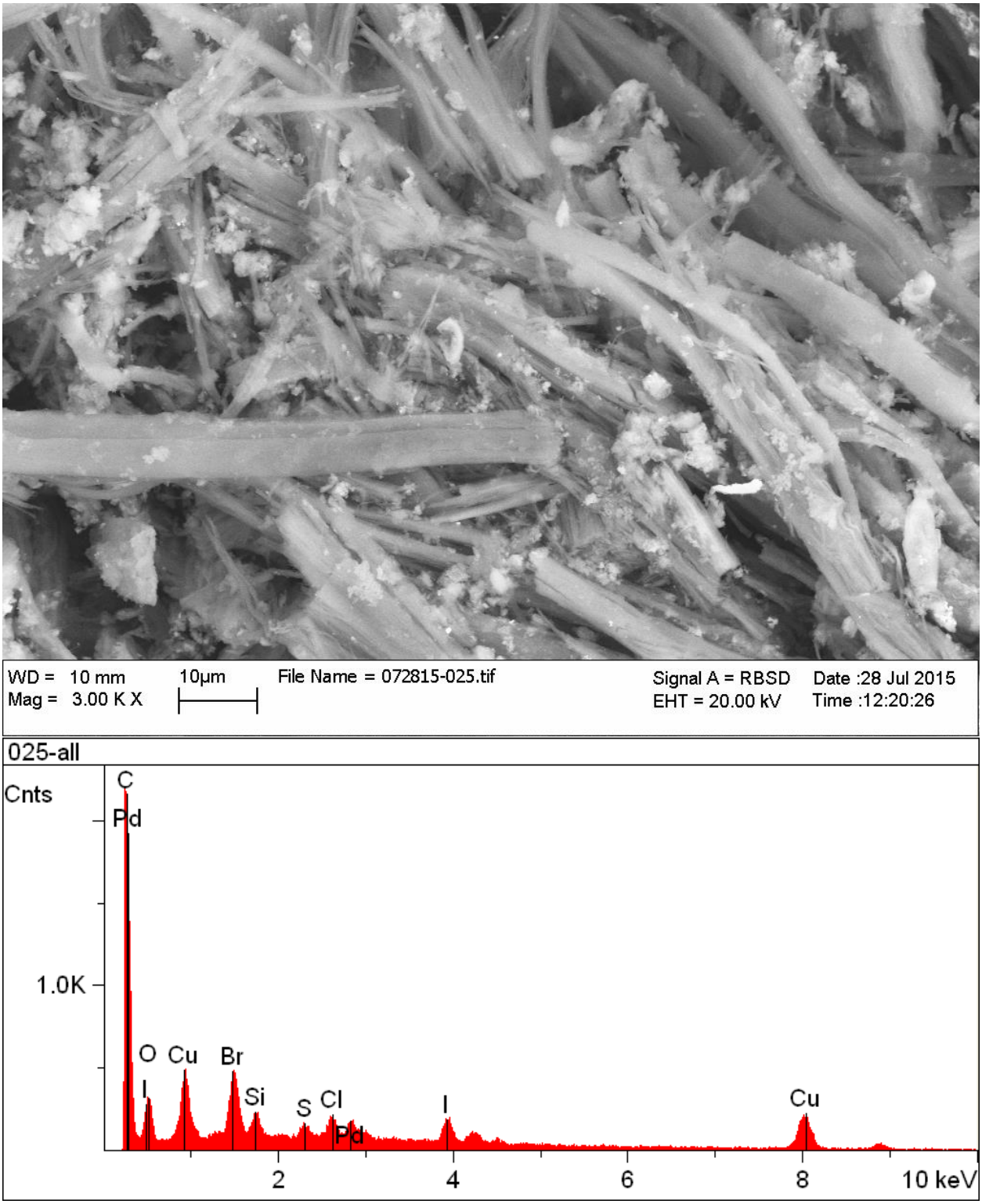


Figure 4.5 SEM and EDS spectrum of reacted PBDA cocrystal after Sonogashira Reaction

Since room temperature reaction was not successful, another reaction was tried with higher temperature. Using PBDA cocrystal as starting material, the Sonogashira reaction temperature was increased to 80°C. After 24-48 hours, the cocrystal fiber turned into black powder. Palladium salts were filtered by water extraction and home-couple of TMS-acetylene was removed with organic solvent after centrifugation to give black powder. SEM and EDS spectrums were collected afterwards. (Fig 4.6)

The SEM spectrum shows a dark material which implies lower conductivity and small element. Compared to the previous SEM image, this one indicates the smaller amount of bromine. EDS spectrum also confirms the lower ratio of bromine to carbon. It is believed bromine was removed during Sonogashira reaction. The reaction of PBDA at high temperature decomposed the polymer.

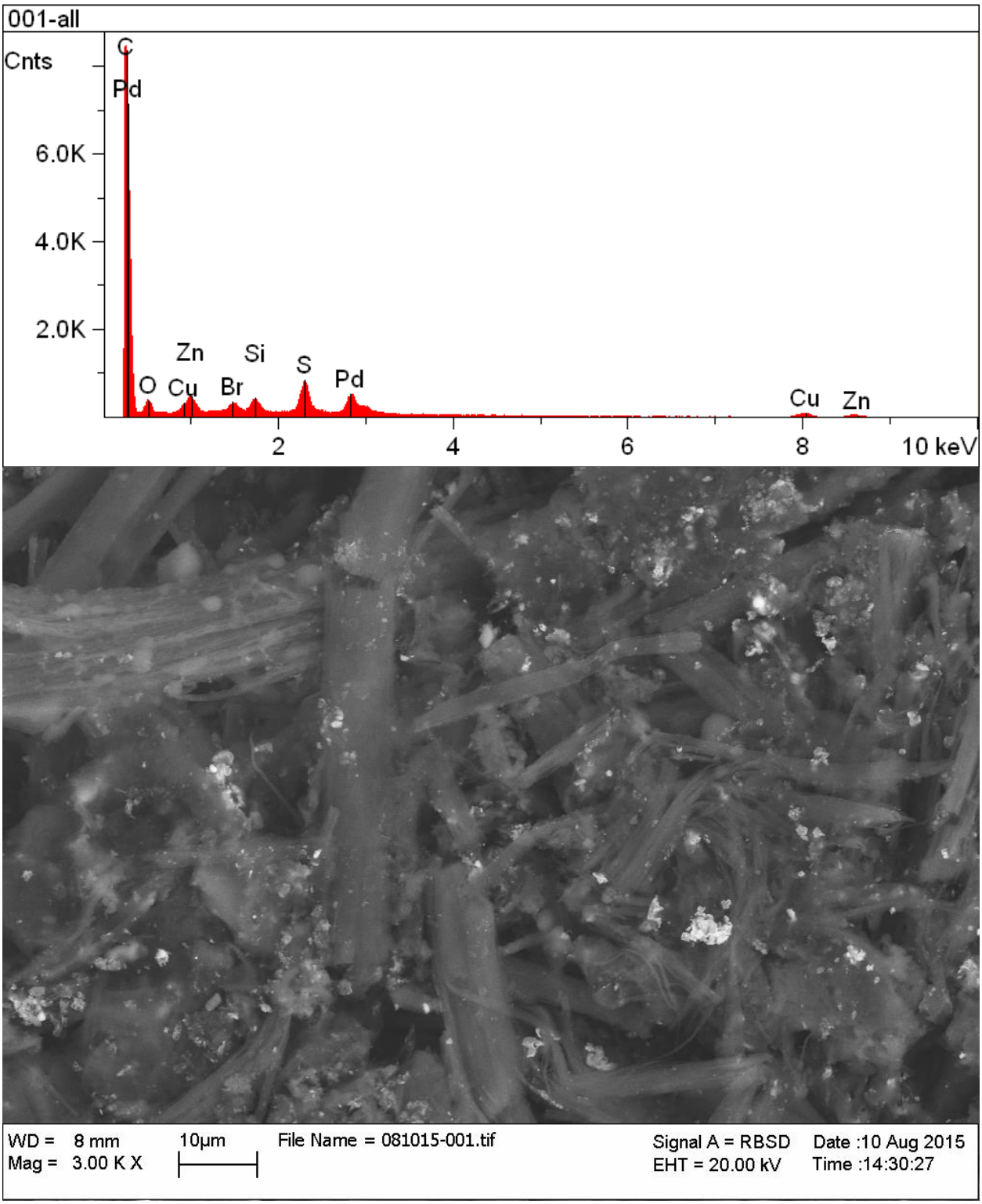
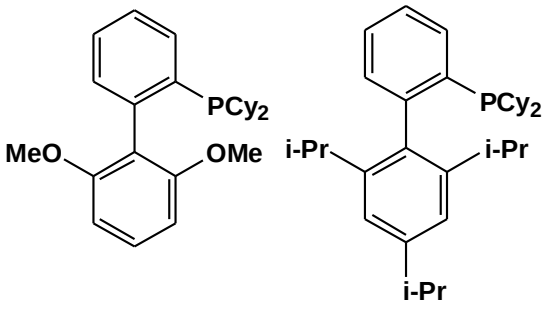


Figure 4.6 SEM and EDS spectrum of reacted PBDA cocrystal after Sonogashira Reaction

From the above experiments, it is believed 80 °C is too high for the polymer. Another reaction was performed with PBDA cocrystal at 50 °C. However, PBDA was eliminated again based on SEM and EDS spectrums. Polymer did not survive at 50 °C.

After all these unsuccessful experiment, it was believed the normal common-used catalysts need to be replaced with highly reactive catalysts. Since there were no reported similar reactions on dibromoalkenes, Sonogashira or Suzuki reactions on arylchloride and vinylchloride were searched. It is believed once the reaction could work on chloride compound which has almost the lowest reactivity among halogen atoms, it is highly possible dibromoalkene could work under similar catalyst system. The Stephen Buchwald group did a substantial work on high efficient catalyst system.[45] Utilizing the palladium precatalyst and dialkylphosphine ligands **30** and **31** (Fig 4.7) for the Suzuki-Miyaura reaction, many reaction which usually

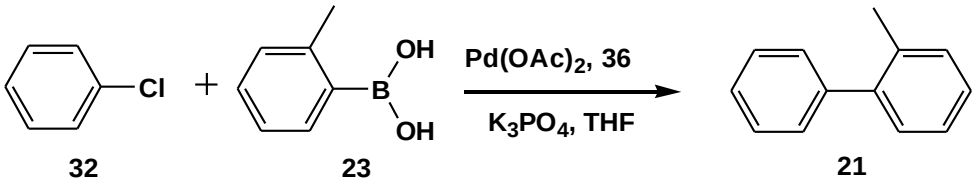


30 **31**

Figure 4.7 SPhos and XPhos

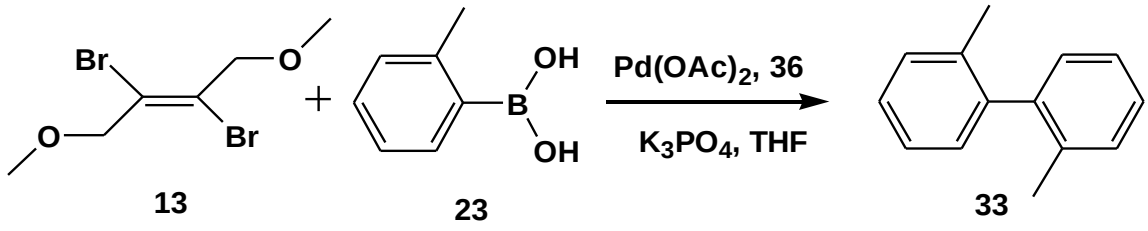
requires high temperature can be processed at room temperature.

This highly efficient catalyst system requires strictly experimental set up. All the starting materials, solvents and catalysts have been processed to be oxygen free. All the solvents, reagents, reactant and catalyst solution were degased by Freeze-Pump-Thaw 3 times. The first time experiment failed and the second trial succeed to afford compound **21**.[45b] (Scheme 4.14)



Scheme 4.14 Suzuki reaction of **32** and **23** afforded **33**[43b]

The same reaction condition was used on model compound **13**. Unfortunately the reaction still did not work. Starting material **13** was recovered. Tolylboronic acid **23** home-coupled to a byproduct **33**. (Scheme 4.15)

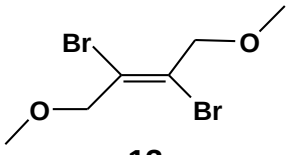


Scheme 4.15 Suzuki reaction of **13** and **23** afforded **34**

4.5 Future experiments.

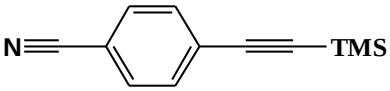
It is very difficult to run post-polymerization reaction. The reaction conditions vary with different compounds. The characterization is also very difficult. The future experiment will be focused on UV, IR or Raman spectroscopy active compounds. Using these compounds, the reaction results could be determined right away by IR which gives convenience for a variety of small quantity model reaction experiment tests.

4.6 Experimental



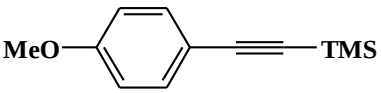
13

Scheme 4.2, Compound 13: Trans-2,3-Dibromo-2-butene-1,4-diol **12** (246 mg, 1 mmol) was dissolved in 30 mL THF and the mixture was stirred for 5 minutes. Methyl iodine (568 mg, 4 mmol) was added into the solution. Potassium tert-butoxide (448 mg, 4 mmol) was added. The mixture turned from clear to cloudy immediately and was stirred for overnight. The solvent was *vacuo* removed at room temperature. A short plug (SiO_2/ethyl acetate : hexane = 1 : 5) was used to afford a yellow oil. The product weighed 123 mg (90%). ^{13}C NMR (400 MHz, $CDCl_3$) δ 121.85, 75.56, 57.79.[46]



16

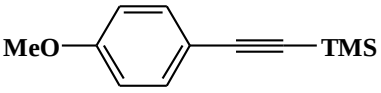
Scheme 4.3, Compound 16: 4-cyano-1-iodobenzene (115 mg, 0.5 mmol) and $PdCl_2(PPh3)_2$ (17 mg, 0.025 mmol) were placed into a round-bottom flask and pumped 15 minutes to vacuum the flask. The flask was then refilled with argon. The same procedure was repeated 3 times to ensure oxygen-free environment. Trimethylsilylacetylene (58.9 mg, 0.6 mmol) and triethylamine (3 mL, 21.5 mmol) were added and stirred for 15 minutes. CuI (4.8 mg, 0.025 mmol) was added at last. The mixture was stirred for overnight. The reaction mixture was rotary evaporated at room temperature. A short plug (SiO_2/ethyl acetate : hexane = 1 : 10) was used to afford a yellow solid. ^{13}C NMR (400 MHz, $CDCl_3$) δ 132.35, 131.84, 127.90,118.32, 111.68, 99.46, -0.35.



18

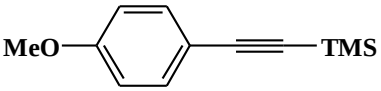
Scheme 4.4, Compound 18, Entry 1: 4-methoxy-1-iodobenzene **17** (115 mg, 0.5 mmol) and $PdCl_2(PPh_3)_2$ (17 mg, 0.025 mmol) were placed into a round-bottom flask. The round-bottom flask was pumped 15 minutes and refilled with argon. The procedure was repeated 3 times. Trimethylsilylacetylene (58.9 mg, 0.6 mmol), triethylamine (3 mL, 21.5 mmol) and THF 20 mL were added and stirred for 15

minutes. CuI (4.8 mg, 0.025 mmol) was added at last. The mixture was heated to 45 °C and stirred for overnight. The reaction mixture was rotary evaporated at room temperature. A short plug (SiO_2/ethyl acetate : hexane = 1 : 10) was used to afford a yellow oil. The product weighed 91.5 mg (90%). ^{13}C NMR (400 MHz, $CDCl_3$) δ -0.6, 55.0, 92.2, 105.2, 113.7, 115.2, 133.4, 159.7.[40]



18

Scheme 4.4, Compound 18, Entry 2: 4-methoxy-1-bromobenzene 19 (94 mg, 0.5 mmol) and $PdCl_2(PPh_3)_2$ (17 mg, 0.025 mmol) were placed into a round-bottom flask. The round-bottom flask was pumped 15 minutes and refilled with argon. The procedure was repeated 3 times. Trimethylsilylacetylene (58.9 mg, 0.6 mmol), triethylamine (3 mL, 21.5 mmol) and THF 20 mL were added and stirred for 15 minutes. CuI (4.8 mg, 0.025 mmol) was added at last. The mixture was heated to 45 °C and stirred for overnight. The reaction mixture was rotary evaporated at room temperature. A short plug (SiO_2/ethyl acetate : hexane = 1 : 10) was used to afford a yellow oil. The product weighed 20.1 mg (20%). ^{13}C NMR (400 MHz, $CDCl_3$) δ -0.6, 55.0, 92.2, 105.2, 113.7, 115.2, 133.4, 159.7.[40]



18

Scheme 4.4, Compound 18, Entry 3: The procedure is the same as entry 2. The only difference is the reaction temperature. In this experiment, the temperature was increased from 45 °C to 80 °C. The product weighed 82.2 mg (80%). ^{13}C NMR (400 MHz, $CDCl_3$) δ -0.6, 55.0, 92.2, 105.2, 113.7, 115.2, 133.4, 159.7.[40]

Table 4.1, Entry 1: Trans-2,3-Dibromo-2-butene-1,4-dimethoxy **13** (137 mg, 0.5 mmol) and $PdCl_2(PPh_3)_2$ (17 mg, 0.025 mmol) were placed into a round-bottom flask. The round-bottom flask was pumped 15 minutes and refilled with argon. The procedure was repeated 3 times. Trimethylsilylacetylene (58.9 mg, 0.6 mmol), triethylamine (3 mL, 21.5 mmol) and THF 20 mL were added and stirred for 15 minutes. CuI (4.8 mg, 0.025 mmol) was added at last. The mixture was stirred at room temperature for overnight. The reaction mixture was rotary evaporated at room temperature. A short plug (SiO_2/ethyl acetate : hexane = 1 : 10) was used to recover the starting material.

Table 4.1, Entry 2–4: The procedure was the same as entry 1. The only difference in each entry is the base. Diisopropylamine was used in Entry 2. n-Butylamine was used in Entry 3. Potassium tert-butoxide as used in Entry 4. Starting materials were all recovered in these three experiments.

Table 4.1, Entry 5: Trans-2,3-Dibromo-2-butene-1,4-dimethoxy **13** (137 mg, 0.5 mmol) and $PdCl_2(PPh_3)_2$ (17 mg, 0.025 mmol) were placed into a round-bottom flask. The round-bottom flask was pumped 15 minutes and refilled with argon. The procedure was repeated 3 times. Trimethylsilylacetylene (58.9 mg, 0.6 mmol), triethylamine (3 mL, 21.5 mmol) and THF 20 mL were added and stirred for 15 minutes. CuI (4.8 mg, 0.025 mmol) was added at last. The mixture was heated to 80 °C and stirred for overnight. The reaction mixture was rotary evaporated at room temperature. A short plug ($_{SiO2}$/ethyl acetate : hexane = 1 : 10) was used to afford 1,4-dimethoxy-2-butyne. The product weighed 52.4 mg (92%). ^{13}C NMR (400 MHz, $CDCl_3$) δ 82.22, 59.79, 57.52.

Table 4.1, Entry 6–8: The procedure was the same as entry 5. The only difference in each entry is the base. Diisopropylamine was used in Entry 6. n-Butylamine was used in Entry 7. Potassium tert-butoxide as used in Entry 8. 1,4-dimethoxy-2-butynes (90%) were obtained in these three experiments.

Table 4.1, Entry 9: Trans-2,3-Dibromo-2-butene-1,4-dimethoxy **13** (137 mg, 0.5 mmol) and $PdCl_2(PPh_3)_2$ (17 mg, 0.025 mmol) were placed into a round-bottom flask. The round-bottom flask was pumped 15 minutes and refilled with argon. The procedure was repeated 3 times. Trimethylsilylacetylene (58.9 mg, 0.6 mmol),

triethylamine (3 mL, 21.5 mmol) and THF 20 mL were added and stirred for 15 minutes. CuI (4.8 mg, 0.025 mmol) was added at last. The mixture was heated to 60 °C and stirred for overnight. The reaction mixture was rotary evaporated at room temperature. A short plug (SiO_2/ethyl acetate : hexane = 1 : 10) was used to afford 1,4-dimethoxy-2-butyne. The product weighed 52.4 mg (92%). ^{13}C NMR (400 MHz, $CDCl_3$) δ 82.22, 59.79, 57.52.

Table 4.1, Entry 10–12: The procedure was the same as entry 9. The only difference in each entry is the base. Diisopropylamine was used in Entry 10. n-Butylamine was used in Entry 11. Potassium tert-butoxide as used in Entry 12. 1,4-dimethoxy-2-butynes (90%) were obtained in these three experiments.

Table 4.1, Entry 13: Trans-2,3-Dibromo-2-butene-1,4-dimethoxy **13** (137 mg, 0.5 mmol) and $PdCl_2(PPh_3)_2$ (17 mg, 0.025 mmol) were placed into a round-bottom flask. The round-bottom flask was pumped 15 minutes and refilled with argon. The procedure was repeated 3 times. Trimethylsilylacetylene (58.9 mg, 0.6 mmol), triethylamine (3 mL, 21.5 mmol) and THF 20 mL were added and stirred for 15 minutes. CuI (4.8 mg, 0.025 mmol) was added at last. The mixture was heated to 40 °C and stirred for overnight. The reaction mixture was rotary evaporated at room temperature. A short plug (SiO_2/ethyl acetate : hexane = 1 : 10) was used to recover the starting material.

Table 4.1, Entry 14–16: The procedure was the same as entry 13. The only difference in each entry is the base. Diisopropylamine was used in Entry 14. n-Butylamine was used in Entry 15. Potassium tert-butoxide as used in Entry 16. Starting materials were all recovered in these three experiments.

Table 4.2, Entry 1: Trans-2,3-Dibromo-2-butene-1,4-dimethoxy **13** (137 mg, 0.5 mmol) and $PdCl_2(PPh_3)_2$ (17 mg, 0.025 mmol) were placed into a round-bottom flask. The round-bottom flask was pumped 15 minutes and refilled with argon. The procedure was repeated 3 times. (Triisopropylsilyl)acetylene (109.4 mg, 0.6 mmol), triethylamine (3 mL, 21.5 mmol) and THF 20 mL were added and stirred for 15 minutes. CuI (4.8 mg, 0.025 mmol) was added at last. The mixture was stirred at room temperature for overnight. The reaction mixture was rotary evaporated at room temperature. A short plug (SiO_2/ethyl acetate : hexane = 1 : 10) was used to recover the starting material.

Table 4.2, Entry 2–4: The procedure was the same as entry 1. The only difference in each entry is the base. Diisopropylamine was used in Entry 2. n-Butylamine was used in Entry 3. Potassium tert-butoxide as used in Entry 4. Starting materials were all recovered in these three experiments.

Table 4.2, Entry 5: Trans-2,3-Dibromo-2-butene-1,4-dimethoxy **13** (137 mg, 0.5 mmol) and $PdCl_2(PPh_3)_2$ (17 mg, 0.025 mmol) were placed into a round-bottom

flask. The round-bottom flask was pumped 15 minutes and refilled with argon. The procedure was repeated 3 times. (Triisopropylsilyl)acetylene (109.4 mg, 0.6 mmol), triethylamine (3 mL, 21.5 mmol) and THF 20 mL were added and stirred for 15 minutes. CuI (4.8 mg, 0.025 mmol) was added at last. The mixture was heated to 80 °C and stirred for overnight. The reaction mixture was rotary evaporated at room temperature. A short plug (SiO_2/ethyl acetate : hexane = 1 : 10) was used to afford 1,4-dimethoxy-2-butyne. The product weighed 52.4 mg (92%). ^{13}C NMR (400 MHz, $CDCl_3$) δ 82.22, 59.79, 57.52.

Table 4.2, Entry 6–8: The procedure was the same as entry 5. The only difference in each entry is the base. Diisopropylamine was used in Entry 6. n-Butylamine was used in Entry 7. Potassium tert-butoxide as used in Entry 8. 1,4-dimethoxy-2-butynes (90%) were obtained in these three experiments.

Table 4.2, Entry 9: Trans-2,3-Dibromo-2-butene-1,4-dimethoxy **13** (137 mg, 0.5 mmol) and $PdCl_2(PPh_3)_2$ (17 mg, 0.025 mmol) were placed into a round-bottom flask. The round-bottom flask was pumped 15 minutes and refilled with argon. The procedure was repeated 3 times. (Triisopropylsilyl)acetylene (109.4 mg, 0.6 mmol), triethylamine (3 mL, 21.5 mmol) and THF 20 mL were added and stirred for 15 minutes. CuI (4.8 mg, 0.025 mmol) was added at last. The mixture was

heated to 60 °C and stirred for overnight. The reaction mixture was rotary evaporated at room temperature. A short plug (SiO_2/ethyl acetate : hexane = 1 : 10) was used to afford 1,4-dimethoxy-2-butyne. The product weighed 52.4 mg (92%). ^{13}C NMR (400 MHz, $CDCl_3$) δ 82.22, 59.79, 57.52.

Table 4.2, Entry 10–12: The procedure was the same as entry 9. The only difference in each entry is the base. Diisopropylamine was used in Entry 10. n-Butylamine was used in Entry 11. Potassium tert-butoxide as used in Entry 12. 1,4-dimethoxy-2-butynes (90%) were obtained in these three experiments.

Table 4.2, Entry 13: Trans-2,3-Dibromo-2-butene-1,4-dimethoxy **13** (137 mg, 0.5 mmol) and $PdCl_2(PPh_3)_2$ (17 mg, 0.025 mmol) were placed into a round-bottom flask. The round-bottom flask was pumped 15 minutes and refilled with argon. The procedure was repeated 3 times. (Triisopropylsilyl)acetylene (109.4 mg, 0.6 mmol), triethylamine (3 mL, 21.5 mmol) and THF 20 mL were added and stirred for 15 minutes. CuI (4.8 mg, 0.025 mmol) was added at last. The mixture was heated to 40 °C and stirred for overnight. The reaction mixture was rotary evaporated at room temperature. A short plug (SiO_2/ethyl acetate : hexane = 1 : 10) was used to recover the starting material.

Table 4.2, Entry 14–16: The procedure was the same as entry 13. The only difference in each entry is the base. Diisopropylamine was used in Entry 14. n-

Butylamine was used in Entry 15. Potassium tert-butoxide as used in Entry 16. Starting materials were all recovered in these three experiments.

Table 4.3, Entry 1: Trans-2,3-Dibromo-2-butene-1,4-dimethoxy **13** (137 mg, 0.5 mmol) and $PdCl_2(PPh_3)_2$ (17 mg, 0.025 mmol) were placed into a round-bottom flask. The round-bottom flask was pumped 15 minutes and refilled with argon. The procedure was repeated 3 times. Phenylacetylene (61.2 mg, 0.6 mmol), triethylamine (3 mL, 21.5 mmol) and THF 20 mL were added and stirred for 15 minutes. CuI (4.8 mg, 0.025 mmol) was added at last. The mixture was stirred at room temperature for overnight. The reaction mixture was rotary evaporated at room temperature. A short plug (SiO_2/ethyl acetate : hexane = 1 : 10) was used to recover the starting material.

Table 4.3, Entry 2–4: The procedure was the same as entry 1. The only difference in each entry is the base. Diisopropylamine was used in Entry 2. n-Butylamine was used in Entry 3. Potassium tert-butoxide as used in Entry 4. Starting materials were all recovered in these three experiments.

Table 4.3, Entry 5: Trans-2,3-Dibromo-2-butene-1,4-dimethoxy **13** (137 mg, 0.5 mmol) and $PdCl_2(PPh_3)_2$ (17 mg, 0.025 mmol) were placed into a round-bottom flask. The round-bottom flask was pumped 15 minutes and refilled with argon. The procedure was repeated 3 times. Phenylacetylene (61.2 mg, 0.6 mmol),

triethylamine (3 mL, 21.5 mmol) and THF 20 mL were added and stirred for 15 minutes. CuI (4.8 mg, 0.025 mmol) was added at last. The mixture was heated to 80 °C and stirred for overnight. The reaction mixture was rotary evaporated at room temperature. A short plug (SiO_2/ethyl acetate : hexane = 1 : 10) was used to afford 1,4-dimethoxy-2-butyne. The product weighed 52.4 mg (92%). ^{13}C NMR (400 MHz, $CDCl_3$) δ 82.22, 59.79, 57.52.

Table 4.3, Entry 6–8: The procedure was the same as entry 5. The only difference in each entry is the base. Diisopropylamine was used in Entry 6. n-Butylamine was used in Entry 7. Potassium tert-butoxide as used in Entry 8. 1,4-dimethoxy-2-butynes (90%) were obtained in these three experiments.

Table 4.3, Entry 9: Trans-2,3-Dibromo-2-butene-1,4-dimethoxy **13** (137 mg, 0.5 mmol) and $PdCl_2(PPh_3)_2$ (17 mg, 0.025 mmol) were placed into a round-bottom flask. The round-bottom flask was pumped 15 minutes and refilled with argon. The procedure was repeated 3 times. Phenylacetylene (61.2 mg, 0.6 mmol), triethylamine (3 mL, 21.5 mmol) and THF 20 mL were added and stirred for 15 minutes. CuI (4.8 mg, 0.025 mmol) was added at last. The mixture was heated to 60 °C and stirred for overnight. The reaction mixture was rotary evaporated at room temperature. A short plug (SiO_2/ethyl acetate : hexane = 1 : 10) was used to afford 1,4-dimethoxy-2-butyne. The product weighed 52.4 mg (92%). ^{13}C NMR (400 MHz, $CDCl_3$) δ 82.22, 59.79, 57.52.

Table 4.3, Entry 10–12: The procedure was the same as entry 9. The only difference in each entry is the base. Diisopropylamine was used in Entry 10. n-Butylamine was used in Entry 11. Potassium tert-butoxide as used in Entry 12. 1,4-dimethoxy-2-butynes (90%) were obtained in these three experiments.

Table 4.3, Entry 13: Trans-2,3-Dibromo-2-butene-1,4-dimethoxy **13** (137 mg, 0.5 mmol) and $PdCl_2(PPh_3)_2$ (17 mg, 0.025 mmol) were placed into a round-bottom flask. The round-bottom flask was pumped 15 minutes and refilled with argon. The procedure was repeated 3 times. Phenylacetylene (61.2 mg, 0.6 mmol), triethylamine (3 mL, 21.5 mmol) and THF 20 mL were added and stirred for 15 minutes. CuI (4.8 mg, 0.025 mmol) was added at last. The mixture was heated to 40 °C and stirred for overnight. The reaction mixture was rotary evaporated at room temperature. A short plug (SiO_2/ethyl acetate : hexane = 1 : 10) was used to recover the starting material.

Table 4.3, Entry 14–16: The procedure was the same as entry 13. The only difference in each entry is the base. Diisopropylamine was used in Entry 14. n-Butylamine was used in Entry 15. Potassium tert-butoxide as used in Entry 16. Starting materials were all recovered in these three experiments.

Table 4.4, Entry 1: Trans-4,5-dibromo-4-octene **11** (135 mg, 0.5 mmol) and $PdCl_2(PPh_3)_2$ (17 mg, 0.025 mmol) were placed into a round-bottom flask. The round-bottom flask was pumped 15 minutes and refilled with argon. The procedure was repeated 3 times. Trimethylsilylacetylene (58.9 mg, 0.6 mmol), triethylamine (3 mL, 21.5 mmol) and THF 20 mL were added and stirred for 15 minutes. CuI (4.8 mg, 0.025 mmol) was added at last. The mixture was stirred at room temperature for overnight. The reaction mixture was rotary evaporated at room temperature. A short plug (SiO_2/ethyl acetate : hexane = 1 : 10) was used to recover the starting material.

Table 4.4, Entry 2–4: The procedure was the same as entry 1. The only difference in each entry is the temperature. In Entry 2, the reaction temperature is 80 °C. 4-Octyne was afforded. ^{13}C NMR (400 MHz, $CDCl_3$) 80.22, 22.73, 20.91, 13.51. In entry 3, the reaction temperature is 60 °C. 4-Octyne was afforded. In entry 4, the reaction temperature is 40 °C. The starting material was recovered.

Table 4.4, Entry 5: Trans-4,5-dibromo-4-octene **11** (135 mg, 0.5 mmol) and $PdCl_2(PPh_3)_2$ (17 mg, 0.025 mmol) were placed into a round-bottom flask. The round-bottom flask was pumped 15 minutes and refilled with argon. The procedure was repeated 3 times. Trimethylsilylacetylene (58.9 mg, 0.6 mmol), diisopropylamine (3 mL, 21.3 mmol) and THF 20 mL were added and stirred for 15 minutes. CuI (4.8 mg, 0.025 mmol) was added at last. The mixture was stirred

at room temperature for overnight. The reaction mixture was rotary evaporated at room temperature. A short plug (SiO_2/ethyl acetate : hexane = 1 : 10) was used to recover the starting material.

Table 4.4, Entry 6–8: The procedure was the same as entry 1. The only difference in each entry is the temperature. In Entry 6, the reaction temperature is 80 °C. 4-Octyne was afforded. ^{13}C NMR (400 MHz, $CDCl_3$) 80.22, 22.73, 20.91, 13.51. In entry 7, the reaction temperature is 60 °C. 4-Octyne was afforded. In entry 8, the reaction temperature is 40 °C. The starting material was recovered.

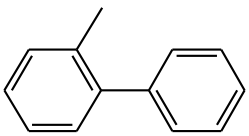
Table 4.5, Entry 1: Trans-2,3-dibromo-2-diol **12** (123 mg, 0.5 mmol) and $PdCl_2(PPh_3)_2$ (17 mg, 0.025 mmol) were placed into a round-bottom . The round-bottom flask was pumped 15 minutes and refilled with argon. The procedure was repeated 3 times. Trimethylsilylacetylene (58.9 mg, 0.6 mmol), triethylamine (3 mL, 21.5 mmol) and THF 20 mL were added and stirred for 15 minutes. CuI (4.8 mg, 0.025 mmol) was added at last. The mixture was stirred at room temperature for overnight. The reaction mixture was rotary evaporated at room temperature. A short plug (SiO_2/ethyl acetate : hexane = 1 : 10) was used to recover the starting material.

Table 4.5, Entry 2–4: The procedure was the same as entry 1. The only difference in each entry is the temperature. In Entry 2, the reaction temperature is 80 °C. 4-

Octyne was afforded. ^{13}C NMR (400 MHz, $CDCl_3$) 80.22, 22.73, 20.91, 13.51. In entry 3, the reaction temperature is 60 °C. 4-Octyne was afforded. In entry 4, the reaction temperature is 40 °C. The starting material was recovered.

Table 4.5, Entry 5: Trans-2,3-dibromo-2-diol **12** (123 mg, 0.5 mmol) and $PdCl_2(PPh_3)_2$ (17 mg, 0.025 mmol) were placed into a round-bottom flask. The round-bottom flask was pumped 15 minutes and refilled with argon. The procedure was repeated 3 times. Trimethylsilylacetylene (58.9 mg, 0.6 mmol), diisopropylamine (3 mL, 21.3 mmol) and THF 20 mL were added and stirred for 15 minutes. CuI (4.8 mg, 0.025 mmol) was added at last. The mixture was stirred at room temperature for overnight. The reaction mixture was rotary evaporated at room temperature. A short plug ($_{SiO2}$/ethyl acetate : hexane = 1 : 10) was used to recover the starting material.

Table 4.5, Entry 6–8: The procedure was the same as entry 5. The only difference in each entry is the temperature. In Entry 6, the reaction temperature is 80 °C. 4-Octyne was afforded. ^{13}C NMR (400 MHz, $CDCl_3$) 80.22, 22.73, 20.91, 13.51. In entry 7, the reaction temperature is 60 °C. 4-Octyne was afforded. In entry 8, the reaction temperature is 40 °C. The starting material was recovered.



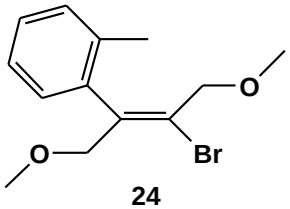
21

Scheme 4.5, 2-phenyltoluene 21: In a grove box, bromotolene **19** (344 mg, 2 mmol), phenylboronic acid **20** (272 mg, 2.2 mmol) and KF (300 mg, 5.17 mmol) were added to a 7-mL vial, which was charged with a stir bar. 1.8 mL THF, $Pd_2(dba)_3$ (33 mg, 0.318 mmol) and $P(t\text{-}Bu)_3$ (16 mg, 0.079 mmol) were added into the vial at room temperature and stirred for 24 hours. The reaction mixture was quenched with Et_2O, filtered through a short plug (SiO_2/ethyl acetate). The solution was rotary evaporated to afford the final product as a colorless liquid (93%). ^{13}C NMR (400 MHz, $CDCl_3$) δ 141.01, 141.97, 135.27, 130.27, 129.77, 129.16, 128.04, 127.21, 126.72, 125.73, 20.39. [41]

Scheme 4.6: In a grove box, trans-4,5-dibromo-4-octene **11** (135 mg, 0.5 mmol), phenylboronic acid **20** (133 mg, 1.1 mmol) and KF (191.4 mg, 3.3 mmol) were added to a 7-mL vial, which was charged with a stir bar. 1.8 mL THF, $Pd_2(dba)_3$ (9.15 mg, 0.01 mmol) and $P(t\text{-}Bu)_3$ (4.89 mg, 0.024 mmol) were added into the vial at room temperature and stirred for 24 hours. The reaction mixture was quenched with Et_2O, filtered through a short plug (SiO_2/ethyl acetate). The solution was rotary evaporated to recover the starting material.

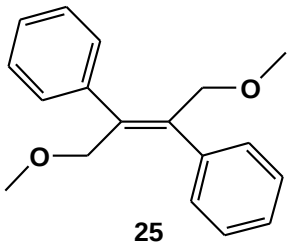
Scheme 4.7: In a grove box, trans-2,3-dibromo-4- Octene 11 (272 mg, 1.0 mmol), phenylboronic acid 20 (268.1 mg, 2.2 mmol) and KF (382.8 mg, 6.6 mmol) were added to a 7-mL vial, which is charged with a stir bar. THF 1.8 mL, $Pd_2(dba)_3$ (45.75 mg, 0.05 mmol) and P(t-Bu)3 (24.48 mg, 0.12 mmol) were added into the

vial at room temperature and stirred for 24 hours. The reaction mixture was quenched with Et2O, filtered through a short plug (SiO2/ethyl acetate). The solution was rotary evaporated to recover the starting material.



24

Scheme 4.8, Entry 1: In a grove box, trans-2,3-dibromo-2-butene-1,4-dimethoxy **13** (270 mg, 1.0 mmol), p-tolylboronic acid **23** (299.2 mg, 2.2 mmol) and KF (382.8 mg, 6.6 mmol) were added to a 7-mL vial, which is charged with a stir bar. THF 1.8 mL, $Pd_2(dba)_3$ (45.75 mg, 0.05 mmol) and $P(t\text{-}Bu)_3$ (24.48 mg, 0.12 mmol) were added into the vial at room temperature and stirred for 24 hours. The reaction mixture was quenched with Et_2O, filtered through a short plug (SiO_2/ethyl acetate). The solution was rotary evaporated to afford compound **24**. The product weighed 170 mg (60%).



25

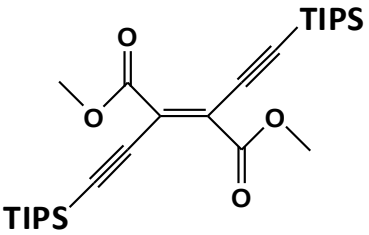
Scheme 4.8, Entry 2: In a grove box, trans-2,3-dibromo-2-butene-1,4-dimethoxy **13** (270 mg, 1.0 mmol), phenylboronic acid **20** (268.4 mg, 2.2 mmol) and KF

(382.8 mg, 6.6 mmol) were added to a 7-mL vial, which is charged with a stir bar. THF 1.8 mL, $Pd_2(dba)_3$ (45.75 mg, 0.05 mmol) and $P(t\text{-}Bu)_3$ (24.48 mg, 0.12 mmol) were added into the vial at room temperature and stirred for 24 hours. The reaction mixture was quenched with Et_2O, filtered through a short plug (SiO_2/ethyl acetate). The solution was rotary evaporated to afford compound **25**. The product weighed 192 mg (72%).

Scheme 4.9: In a grove box, PBDA cocrystal (20.8 mg, 0.1 mmol), p-tolylboronic acid **23** (30 mg, 0.22 mmol) and KF (38.3 mg, 0.66 mmol) were added to a 7-mL vial, which is charged with a stir bar. THF 1 mL, $Pd_2(dba)_3$ (4.57 mg, 0.005 mmol) and $P(t\text{-}Bu)_3$ (2.45 mg, 0.012 mmol) were added into the vial at room temperature and stirred for 24 hours. The reaction mixture was quenched with Et_2O, filtered through a short plug (SiO_2/ethyl acetate). The reacted unknown compound was left on the filter paper for further analysis.

Scheme 4.10, Entry 1: In a grove box, trans-2,3-Dibromo-2-butene-1,4-dimethoxy **13** (270 mg, 1.0 mmol), n-pentyl boronic acid **24** (253 mg, 2.2 mmol) and KF (382.8 mg, 6.6 mmol) were added to a 7-mL vial, which is charged with a stir bar. THF 1.8 mL, $Pd_2(dba)_3$ (45.75 mg, 0.05 mmol) and $P(t\text{-}Bu)_3$ (24.48 mg, 0.12 mmol) were added into the vial at room temperature and stirred for 24 hours. The reaction mixture was quenched with Et_2O, filtered through a short plug (SiO_2/ethyl acetate). The solution was rotary evaporated to recover the starting material.

Scheme 4.10, Entry 2: In a glove box, trans-2,3-Dibromo-2-butene-1,4-dimethoxy **13** (135 mg, 0.5 mmol), 4-N-pentylphenylboronic acid **25** (211.2 mg, 1.1 mmol) and KF (191.9 mg, 3.3 mmol) were added to a 7-mL vial, which is charged with a stir bar. THF 1 mL, $Pd_2(dba)_3$ (23.3 mg, 0.025 mmol) and $P(t\text{-}Bu)_3$ (12.3 mg, 0.06 mmol) were added into the vial at room temperature and stirred for 24 hours. The reaction mixture was quenched with Et_2O, filtered through a short plug (SiO_2/ethyl acetate). The solution was rotary evaporated to recover the starting material.



27

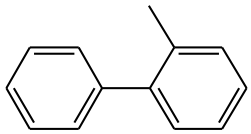
Scheme 4.11, Compound 26: Compound **26** (111 mg, 0.5 mmol) and $PdCl_2(PPh_3)_2$ (17 mg, 0.025 mmol) were placed into a round-bottom flask. The round-bottom flask was pumped 15 minutes and refilled with argon. The procedure was repeated 3 times. (Triisopropylsilyl)acetylene (200 mg, 1.1 mmol) and triethylamine (3 mL, 22.5 mmol) were added and stirred for 15 minutes. CuI (4.8 mg, 0.025 mmol) was added at last. The mixture was stirred at room temperature for overnight. The reaction mixture was rotary evaporated at room temperature. A short plug (SiO_2/ethyl acetate : hexane = 1 : 10) was used to afford a yellow solid.

^{13}C NMR (400 MHz, $CDCl_3$) δ 163.7, 127.3, 109.8, 100.3, 52.7, 18.5, 11.2.[42]

Scheme 4.12: Compound **28** (129 mg, 0.5 mmol) and $PdCl_2(PPh_3)_2$ (17 mg, 0.025 mmol) were placed into a round-bottom flask. The round-bottom flask was pumped 15 minutes and refilled with argon. The procedure was repeated 3 times. (Triisopropylsilyl)acetylene (200 mg, 1.1 mmol), triethylamine (3 mL, 22.5 mmol) and 1 mL THF were added and stirred for 15 minutes. CuI (4.8 mg, 0.025 mmol) was added at last. The mixture was stirred at room temperature for overnight. The reaction mixture was rotary evaporated at room temperature. A short plug (SiO_2/ethyl acetate : hexane = 1 : 10) was used to recover the starting material and bis(triisopropylsilyl)butadiyne (163 mg, 83%)。

Scheme 4.13, Entry 1: PBDA cocrystal (24.3 mg, 0.05 mmol) and $PdCl_2(PPh_3)_2$ (7.1 mg, 0.01 mmol) were placed into a round-bottom . The round-bottom flask was pumped 15 minutes and refilled with argon. The procedure was repeated 3 times. (Triisopropylsilyl)acetylene (20 mg, 0.11 mmol), triethylamine (0.3 mL, 2.25 mmol) and 1 mL THF were added and stirred for 15 minutes. CuI (4.8 mg, 0.025 mmol) was added at last. The mixture was stirred at room temperature for overnight. The reaction mixture was rotary evaporated at room temperature. A short plug (SiO_2/hexane) was used to afford an unknown mixture.

Scheme 4.14, Entry 2: The procedure was the same as entry 1. The only difference is the starting material. An unknown solid mixture was obtained.



21

Scheme 4.14, 2-Phenyltoluene 21: A separate vial was charged with $Pd(OAc)_2$ (1 mg, 0.004 mmol), X-Phos (6.3 mg, 0.013 mmol) and THF 10 mL. An oven-dried 3-neck round-bottom flask was charged with p-tolylboronic acid (51 mg, 0.37 mmol), K_3PO_4 (151 mg, 0.75 mmol) and chlorobenzene (28 mg, 0.25 mmol). The vial and round-bottom flask were connected by long cannula and they are both freeze-pump 3 times with argon. The mixture of vial was stirred for 15 minutes and was transferred into the round-bottom flask by cannula. The reaction mixture turned from pink to green within 10 minutes and turned from green to black in 2 days. The mixture was quenched by diethylether (30 mL). The mixture was rotary evaporated and a short plug (SiO_2/ethyl acetate) was used to afford a yellow liquid. The product weighed 36.9 mg (88%).

Scheme 4.15: The procedure was the same as scheme 4.13. The only different is the halo-compound. Trans-2,3-Dibromo-2-butene-1,4-dimethoxy **13** was used in scheme 4.14. After the same purification process, compound **13** was recovered.

References:

1. "The 2000 Nobel Prize in Chemistry - Popular Information". Nobelprize.org. http://www.nobelprize.org/nobel_prizes/chemistry/laureates/2000/popular.html/ (accessed Jan 10, 2016
2. (a) Baumgartner, T.; Reau, R. Organophosphorus pi-conjugated materials. *Chem. Rev.* **2006,** *106* (11), 4681-4727; (b) Lo, S. C.; Burn, P. L. Development of dendrimers: Macromolecules for use in organic light-emitting diodes and solar cells. *Chem. Rev.* **2007,** *107* (4), 1097-1116; (c) Menard, E.; Meitl, M. A.; Sun, Y. G.; Park, J. U.; Shir, D. J. L.; Nam, Y. S.; Jeon, S.; Rogers, J. A. Micro- and nanopatterning techniques for organic electronic and optoelectronic systems. *Chem. Rev.* **2007,** *107* (4), 1117-1160; (d) Saragi, T. P. I.; Spehr, T.; Siebert, A.; Fuhrmann-Lieker, T.; Salbeck, J., Spiro compounds for organic optoelectronics. *Chem. Rev.* **2007,** *107* (4), 1011-1065.
3. Gunes, S.; Neugebauer, H.; Sariciftci, N. S. Conjugated polymer-based organic solar cells. *Chem. Rev.* **2007,** *107* (4), 1324-1338.
4. McQuade, D. T.; Pullen, A. E.; Swager, T. M. Conjugated polymer-based chemical sensors. *Chem. Rev.* **2000,** *100* (7), 2537-2574.
5. Allison, J. *Electronic Engineering Semiconductors and devices*. McGraw-Hill Book Company: 1971.
6. van Mullekom, H. A. M.; Vekemans, J.; Havinga, E. E.; Meijer, E. W. Developments in the chemistry and band gap engineering of donor-acceptor substituted conjugated polymers. *Mater. Sci. Eng. R-Rep.* **2001,** *32* (1), 1-40.
7. Norwood, R.; Gangopadhay, P.; Shahin, S. Ultra-thin organic photovoltaics with increased efficiency. **2012**.
8. (a) Chi, D.; Qu, S.; Wang, Z.; Wang, J. High efficiency P3HT:PCBM solar cells with an inserted PCBM layer. *J. Mater. Chem. C* **2014,** *2* (22), 4383-4387; (b) Chen, D. A.; Nakahara, A.; Wei, D. G.; Nordlund, D.; Russell, T. P. P3HT/PCBM bulk heterojunction organic photovoltaics: correlating efficiency and morphology. *Nano Lett.* **2011,** *11* (2), 561-567.
9. Seyler, H.; Subbiah, J.; Jones, D. J.; Holmes, A. B.; Wong, W. W. H. Controlled synthesis of poly(3-hexylthiophene) in continuous flow. *Beilstein J. Org. Chem.* **2013,** *9*, 1492-1500.
10. Koch, F.; Heitz, W. Soluble poly(1,4-phenylenevinylene)s and poly(1,4-phenyleneethynylene)s via suzuki coupling. *Macromol. Chem. Phys.* **1997,** *198* (5), 1531-1544.
11. Pfeiffer, S.; Hörhold, H. H. Synthesis of soluble MEH-PPV and MEH-PPB by horner condensation polymerization. *Synthetic Metals* **1999,** *101* (1–3), 109-110.
12. McDonald, R. N.; Campell, T. W., *J. Am. Chem. Soc.* **1960,** *82*, 4669.
13. Wegner, G. *Z. Naturforsch, Teil B* **1969,** *B24*, 824.
14. Baughman, R. H. *J. Polym. Sci Pt B-Polym. Phys.* **1974,** *12*, 1511-1535.
15. (a) Xi, O. Y.; Fowler, F. W.; Lauher, J. W. Single-crystal-to-single-crystal topochemical polymerizations of a terminal diacetylene: Two remarkable transformations give the same conjugated polymer. *J. Am. Chem. Soc.* **2003,** *125* (41), 12400-12401; (b) Coe, S.; Kane, J. J.; Nguyen, T. L.; Toledo, L. M.; Wininger, E.; Fowler, F. W.; Lauher, J. W. Molecular symmetry and the design of molecular solids: The oxalamide functionality as a persistent hydrogen bonding unit. *J. Am. Chem. Soc.* **1997,** *119* (1), 86-93; (c) Nguyen, T. L.; Fowler, F. W.; Lauher, J. W. Commensurate and incommensurate hydrogen bonds. An exercise in crystal engineering. *J. Am. Chem. Soc.* **2001,** *123* (44), 11057-11064.

16. Lauher, J. W.; Fowler, F. W.; Goroff, N. S. Single-crystal-to-single-crystal topochemical polymerizations by design. *Acc. Chem. Res.* **2008,** *41* (9), 1215-1229.
17. Metrangolo, P.; Resnati, G. Halogen Bonding: A paradigm in supramolecular chemistry. *Chem. Eur. J.* **2001,** *7* (12), 2511-2519.
18. Guthrie, F. XXVIII.-On the iodide of iodammonium. *J. Chem. Soc.* **1863,** *16* (0), 239-244.
19. Hassel, O. Structural aspects of interatomic charge-transfer bonding. *Science* **1970,** *170* (3957), 497-502.
20. Metrangolo, P.; Neukirch, H.; Pilati, T.; Resnati, G. Halogen bonding based recognition processes: A world parallel to hydrogen bonding. *Acc. Chem. Res.* **2005,** *38* (5), 386-395.
21. (a) Goroff, N. S.; Curtis, S. M.; Webb, J. A.; Fowler, F. W.; Lauher, J. W. Designed cocrystals based on the pyridine-iodoalkyne halogen bond. *Org. Lett.* **2005,** *7* (10), 1891-1893; (b) Moss, W. N.; Goroff, N. S. Theoretical analysis of the C-13 NMR of iodoalkynes upon complexation with Lewis bases. *J. Org. Chem.* **2005,** *70* (3), 802-808.
22. Sun, A.; Lauher, J. W.; Goroff, N. S. Preparation of poly(diiododiacetylene), an ordered conjugated polymer of carbon and iodine. *Science* **2006,** *312* (5776), 1030-1034.
23. (a) Resch, D.; Lee, C. H.; Tan, S. Y.; Luo, L.; Goroff, N. S. Mechanism and scope of the base-induced dehalogenation of (E)-diiodoalkenes. *Eur. J. Org. Chem.* **2015,** (4), 730-737; (b) Luo, L.; Resch, D.; Wilhelm, C.; Young, C. N.; Halada, G. P.; Gambino, R. J.; Grey, C. P.; Goroff, N. S. Room-temperature carbonization of poly(diiododiacetylene) by reaction with lewis bases. *J. Am. Chem. Soc.* **2011,** *133* (48), 19274-19277.
24. Luo, L.; Wilhelm, C.; Sun, A. W.; Grey, C. P.; Lauher, J. W.; Goroff, N. S. Poly(diiododiacetylene): Preparation, isolation, and full characterization of a very simple poly(diacetylene). *J. Am. Chem. Soc.* **2008,** *130* (24), 7702-7709.
25. Wilhelm, C.; Boyd, S. A.; Chawda, S.; Fowler, F. W.; Goroff, N. S.; Halada, G. P.; Grey, C. P.; Lauher, J. W.; Luo, L.; Martin, C. D.; Parise, J. B.; Tarabrella, C.; Webb, J. A. Pressure-induced polymerization of diiodobutadiyne in assembled cocrystals. *J. Am. Chem. Soc.* **2008,** *130* (13), 4415-4420.
26. (a) Takeuchi, S.; Schulz, R. C. Topochemical polymerization of 1,6-bis(1-pyrenyloxy)-2,4-hexadiyne and some other diacetylenes. *Makromol Chem-rapid* **1983,** *4* (9), 583-587; (b) Gerasimov, G. N.; Pankratov, A. N.; Orlenko, A. P.; Kozlova, N. V.; Sinevitch, E. A.; Teleshov, E. N. Solid-state polymerization of diacetylenes under the action of outside forces on crystalline monomer lattice. *Makromolekulare Chemie-Macromolecular Symposia* **1989,** *26*, 131-140; (c) Kato, J.; Nakamura, K. Solid-state polymerization of 1,6-dichloro-2,4-hexadiyne under high-pressure. *Kobunshi Ronbunshu* **1990,** *47* (1), 57-61; (d) Tang, B. Z.; Xu, H. Y. Preparation, alignment, and optical properties of soluble poly(phenylacetylene)-wrapped carbon nanotubes. *Macromolecules* **1999,** *32* (8), 2569-2576.
27. https://en.wikipedia.org/wiki/Diamond_anvil_cell#References.
28. Jin, H.; Plonka, A. M.; Parise, J. B.; Goroff, N. S. Pressure induced topochemical polymerization of diiodobutadiyne: a single-crystal-to-single-crystal transformation. *CrystEngComm* **2013,** *15* (16), 3106-3110.
29. Gao, K.; Goroff, N. S. Two new iodine-capped carbon rods. *J. Am. Chem. Soc.* **2000,** *122* (38), 9320-9321.
30. Schauer, C. L.; Matwey, E.; Fowler, F. W.; Lauher, J. W. Controlled spacing of metal atoms via ligand hydrogen bonds. *J. Am. Chem. Soc.* **1997,** *119* (42), 10245-10246.

31. Straus, F.; Kollek, L.; Hauptmann, H. On dihalogene-diacetylene (also II. Announcement on the replacement positive hydrogen using halogenes). *Ber. Dtsch. Chem. Ges.* **1930,** *63*, 1897.
32. Hoheisel, T. N.; Schrettl, S.; Marty, R.; Todorova, T. K.; Corminboeuf, C.; Sienkiewicz, A.; Scopelliti, R.; Schweizer, W. B.; Frauenrath, H. A multistep single-crystal-to-single-crystal bromodiacetylene dimerization. *Nat Chem* **2013,** *5* (4), 327-334.
33. Liu, P.-H.; Li, L.; Webb, J. A.; Zhang, Y.; Goroff, N. S. Tetrabromobutatriene: completing the perhalocumulene series. *Org. Lett.* **2004,** *6* (13), 2081-2083.
34. Klaboe, P.; Klosterjensen, E.; Bjarnov, E.; Christensen, D. H.; Nielsen, O. F. Vibrational-spectra and force-fields of dichlorodiacetylene, dibromodiacetylene and diiododiacetylene. *Spectroc. Acta Pt. A-Molec. Biomolec. Spectr.* **1975,** *31* (7), 931-943.
35. Jin, H.; Young, C. N.; Halada, G. P.; Phillips, B. L.; Goroff, N. S. Synthesis of the stable ordered conjugated polymer poly(dibromodiacetylene) from an explosive monomer. *Angew. Chem. Int. Ed.* **2015,** *54* (49), 14690-14695.
36. Solvent Azeotrope Table. http://www.solvent--recycling.com/azeotrope_1.html (Accessed Jan 3rd, 2016).
37. Dembinski, R.; Bartik, T.; Bartik, B.; Jaeger, M.; Gladysz, J. A. Toward metal-capped one-dimensional carbon allotropes: wirelike c6−c20 polyynediyl chains that span two redox-active (η5-C5Me5)Re(NO)(PPh3) endgroups. *J. Am. Chem. Soc.* **2000,** *122* (5), 810-822.
38. Hanson, K.; Roskop, L.; Djurovich, P. I.; Zahariev, F.; Gordon, M. S.; Thompson, M. E. A Paradigm for blue- or red-shifted absorption of small molecules depending on the site of pi-extension. *J. Am. Chem. Soc.* **2010,** *132* (45), 16247-16255.
39. Ang, X. Synthesis of novel conjugated materials - push-pull conjugated diynes and 1,7-phenanthroline derivatives. Stony Brook University, 2015.
40. DeCicco, R. C. The Synthesis and polymerization behavior of polyynes. Stony Brook University, 2012.
41. Organ, M. G.; Ghasemi, H.; Valente, C. The effect of vicinyl olefinic halogens on cross-coupling reactions using Pd(0) catalysis. *Tetrahedron* **2004,** *60* (42), 9453-9461.
42. (a) Matsuda, T.; Suzuki, K.; Miura, N. Rhodium-catalyzed cross-coupling of alkenyl halides with arylboron compounds. *Adv. Synth. Catal.* **2013,** *355* (17), 3396-3400; (b) Rangel, E. R.; Maya, E. M.; Sanchez, F.; de la Campa, J. G.; Iglesias, M. Palladium-heterogenized porous polyimide materials as effective and recyclable catalysts for reactions in water. *Green Chemistry* **2015,** *17* (1), 466-473; (c) Fristrup, P.; Tanner, D.; Norrby, P. O. Updating the asymmetric osmium-catalyzed dihydroxylation (AD) mnemonic: Q2MM modeling and new kinetic measurements. *Chirality* **2003,** *15* (4), 360-368.
43. Littke, A. F.; Dai, C. Y.; Fu, G. C. Versatile catalysts for the suzuki cross-coupling of arylboronic acids with aryl and vinyl halides and triflates under mild conditions. *J. Am. Chem. Soc.* **2000,** *122* (17), 4020-4028.
44. Anthony, J.; Boldi, A. M.; Rubin, Y.; Hobi, M.; Gramlich, V.; Knobler, C. B.; Seiler, P.; Diederich, F. Tetraethynylethenes: fully cross-conjugated π-electron chromophores and molecular scaffolds for all-carbon networks and carbon-rich nanomaterials. *Helv. Chim. Acta.* **1995,** *78* (1), 13-45.
45. (a) Billingsley, K.; Buchwald, S. L., Highly efficient monophosphine-based catalyst for the palladium-catalyzed suzuki−miyaura reaction of heteroaryl halides and heteroaryl boronic acids and esters. *Journal of the American Chemical Society* **2007,** *129* (11), 3358-3366; (b) Wolfe, J. P.; Singer, R. A.; Yang, B. H.; Buchwald, S. L. Highly active palladium catalysts for suzuki coupling reactions. *J. Am. Chem. Soc.* **1999,** *121* (41), 9550-9561.

46. Kikushima, K.; Moriuchi, T.; Hirao, T. Vanadium-catalyzed oxidative bromination promoted by Brønsted acid or lewis acid. *Tetrahedron* **2010,** *66* (34), 6906-6911.