Electron Deficient (n-Type) Conjugated Polymers

by

Sean Owen Clancy

Abstract

There are relatively few conjugated polymers with n-type conductivity, and even less that are soluble in a range of solvents. Since most polymers have p-type conductivity, a variety of materials with good electron mobilities are needed for a multitude of applications. Two types of electron deficient conjugated polymers are proposed which have backbones similar to a hybrid of both polyphenylenes and poly(phenylene vinylene)s, using imino-heterocycles, and containing amphiphilic solubilizing groups to aid in processability. The synthesis for **Polymer I** involves seven steps from commercially available starting materials, while **Polymer II** requires fourteen steps. Quantum chemical calculations were performed on representative oligomers of both polymers to predict structural and electronic properties.

I. Introduction and Research Objectives

Most semiconductive conjugated polymers conduct positive charges (p-type conductivity) more efficiently than negative charges (n-type conductivity). Positive charges are called holes and exist as radical cations or dications (bipolarons), while negative charges are called electrons and exist as radical anions or solitons. For devices such as light-emitting diodes, light-emitting electrochemical cells, field effect transistors, and solid-state lasers, it is important that there is efficient migration of both species. One method of improving the electron mobilities within a polymer is to incorporate electron deficient heterocycles that contain imine nitrogen atoms, such as pyridines, oxadiazoles, triazoles, triazines, and quinoxalines.[1]

This proposal focuses on two types of conjugated polymers that will facilitate electron transport by incorporating multiple imino-heterocycles into the polymer repeat units. These polymers contain electron deficient moieties bound to arenes having solubilizing groups.

Polymer I as shown in Figure 1 has a polymer backbone structure similar to that of both polyphenylenes (PPPs) and poly(phenylene vinylene)s (PPVs). The repeat unit has three electron deficient heterocycles: one pyrazine and two pyridines. The benzene ring in the repeat unit has two poly(ethylene glycol) (PEG) methyl ether groups attached. These groups should enable the polymer to have amphiphilic solubility, being soluble in both aqueous and organic media.[2]

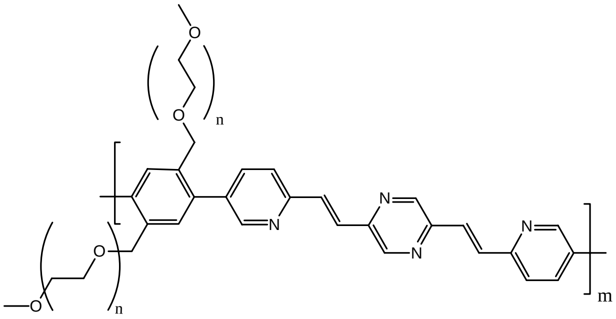


Figure 1. Structure of Polymer I.

Polymer II, as shown in Figure 2, is similar to the structure of **Polymer I**, insofar as the PPV-type units of the polymer are linked to an aryl moiety with a poly(ethylene glycol) methyl ether solubilizing group. A triazole replaces the benzene ring, adding another electron deficient heterocycle to the polymer backbone, thus giving the polymer four electron deficient heterocycles in the repeat unit: one pyrazine, two pyridines, and a triazole. Also, the pyridines face the triazole rather than the pyrazine. The triazole has a PEG group attached to enhance its solubility. The trifluoromethyl group serves as a way to enhance the triazole's electron deficiency, since it is an electron-withdrawing group.

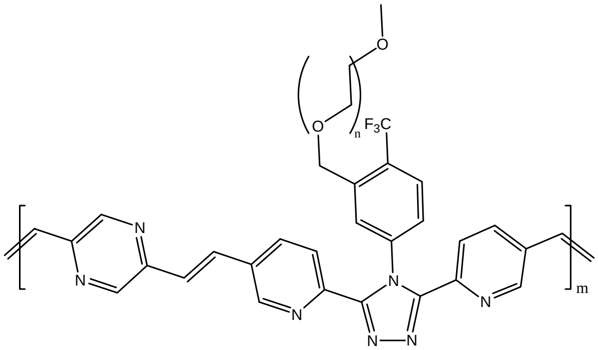


Figure 2. Structure of Polymer II.

II. Computational Chemistry

The electronic and optical properties of a polymer are closely related to its geometrical structure. Geometry optimization calculations were performed at the HF (closed shell) level using the STO-3G basis set in Gaussian 03 to predict some structural properties of the representative oligomers of both polymers, which are shown in Figure 3.[3] As a representation of **Polymer I**, **Trimer I** is predicted to have dihedral angles from 47.0 to 55.4 degrees between 1,4-bis(2-methoxyethoxymethyl)benzenes and their neighboring pyridines. **Trimer II**, which corresponded to **Polymer II**, is predicted to have dihedral angles from 53.3 to 56.3 degrees between the triazoles and their neighboring pyridines. These rotational defects produce "bends" or "kinks" which interrupt and weaken the extent of π-conjugation in a given polymer chain.[4]

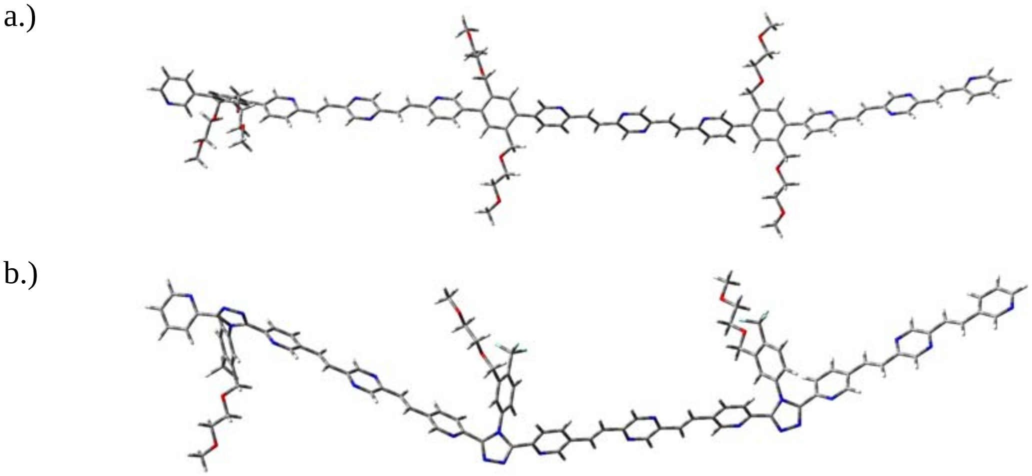


Figure 3. Geometry optimized representations of a.) **Trimer I** and b.) **Trimer II**.

The ideal for a conjugated polymer would be a coplanar system, but a completely planar system is both stabilized by conjugation and destabilized by repulsion due to proximal hydrogen atoms on adjacent rings.[5] In earlier *ab initio* studies, Brédas and coworkers found that torsion angles up to 40 degrees were acceptable for the electronic properties of conjugated polymers, such as polyphenylenes, polypyrroles, and polythiophenes.[6]

Even though the dihedral angles are larger than desired, Figure 4 shows that the molecular orbitals for **Trimer I** are delocalized across all three repeat units for the HOMO (4a), and across two repeat units for the LUMO (4b). This suggests that **Polymer I** should have good electron mobilities throughout the polymer chain.

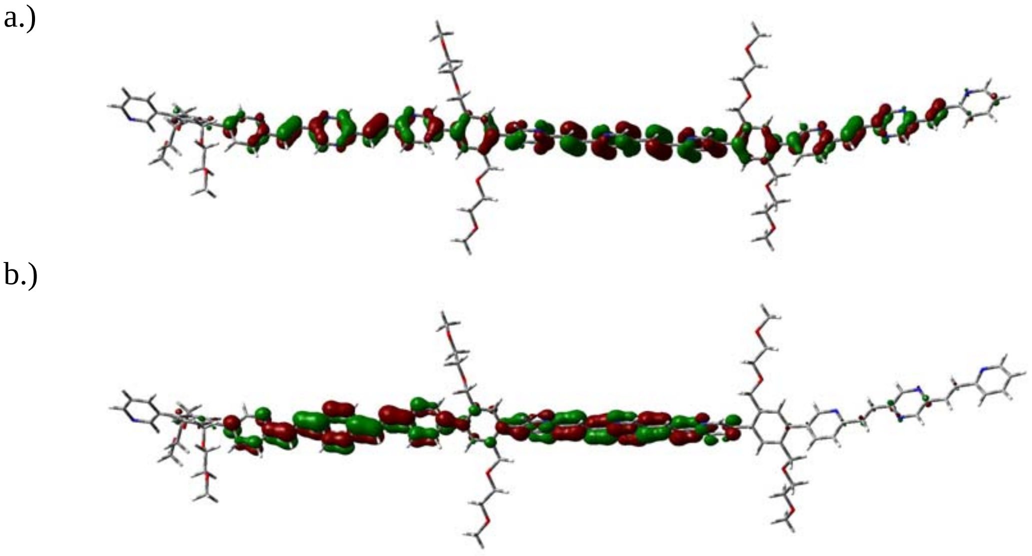


Figure 4. Molecular orbital representations of a.) HOMO and b.) LUMO levels for **Trimer I**.

Although Figure 5 illustrates how the amount of delocalization is comparatively less for **Trimer II**, the electron density is still spread over two repeat units for both the HOMO (5a) and LUMO (5b) states. This suggests that **Polymer II** should also have good electron mobilities, though it may be relatively less than that of **Polymer I**.

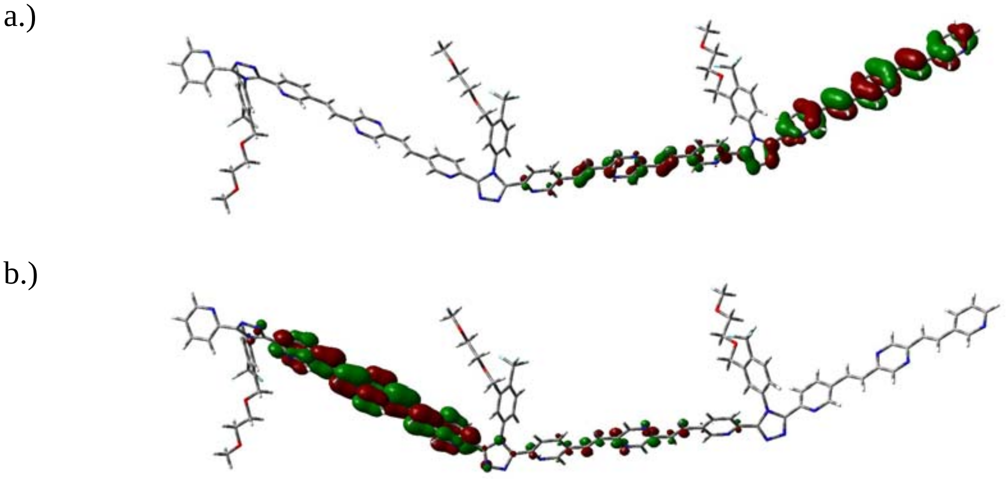


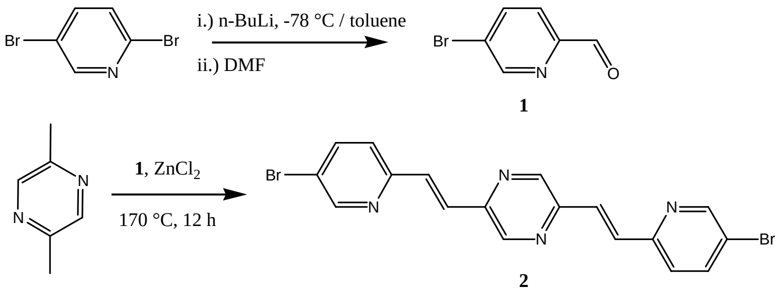
Figure 5. Molecular orbital representations of a.) HOMO and b.) LUMO levels for **Trimer II**.

The size and shape of the majority of the lobes for both **Trimer I** and **Trimer II** are very similar and indicate that most of the electron density is delocalized well across the imino-heterocycle analogs of *p*-distyrylbenzene. The energy differences between the LUMO and HOMO states for **Trimer I** and **Trimer II** are 10.01 eV and 9.96 eV, respectively. These values are larger than expected experimental values, but this is due to the level of approximation the calculations provide. It does show however that the polymers should have similar band gaps.

III. Synthesis

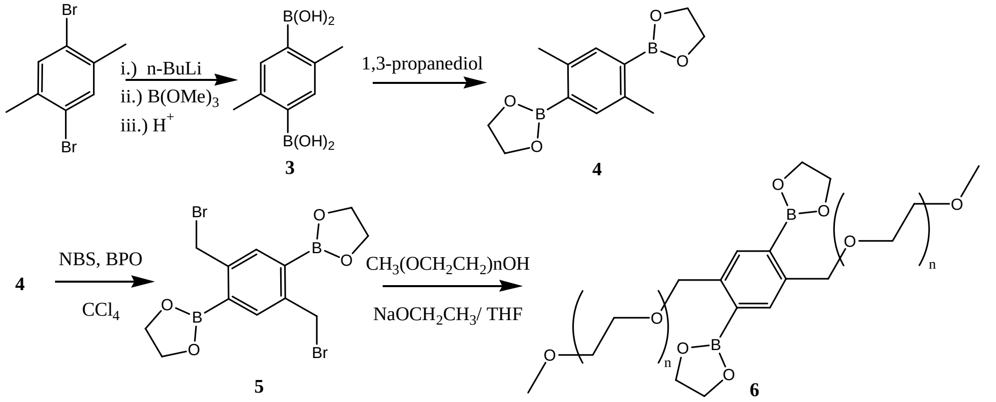
III. A. Polymer I Synthesis

The synthesis of **Polymer I** begins in Scheme 1.1 and is as follows. 2,5-Dibromopyridine is first lithiated with one equivalent of n-butyllithium, followed by the addition of N,N-dimethylformamide, which after a water work-up yields 5-bromopyridine-2-aldehyde (**1**). Compound **1** is reacted with 2,5-dimethylpyrazine in a two to one ratio in the presence of zinc(II) chloride yields 2,5-bis[2-(5-bromo-pyridin-2-yl)-vinyl]pyrazine (**2**).[7] Compound **2** serves as the electron deficient comonomer in **Polymer I**.



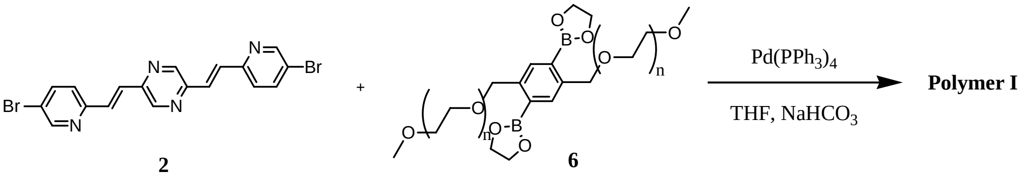
Scheme 1.1. Synthesis of 2,5-bis[2-(5-bromo-pyridin-2-yl)-vinyl]pyrazine.

The other comonomer serves as the solubilizing unit by having two poly(ethylene glycol) methyl ethers attached to a phenyl group, with the synthesis shown in Scheme 1.2. The bromines of 2,5-dibromo-*p*-xylene are converted to boronic acids by first lithiating with n-butyllithium, followed by trimethylborate, and then an aqueous acid work-up, producing 1,4-xylene-2,5-bis(boronic acid) (**3**). The boronic acids are converted to esters by treatment with 1,2-propanediol to give 1,4-xylene-2,5-bis(boronic acid ethanediol ester) (**4**). The methyls are then brominated using N-bromosuccinimide in carbon tetrachloride with a catalytic amount of benzoyl peroxide to yield benzene-2,5-dibromomethyl -1,4-bis(boronic acid ethanediol ester) (**5**).[8] Poly(ethylene glycol) monomethyl ether is then deprotonated using sodium ethoxide in tetrahydrofuran, to which **5** is added, to form the second comonomer, benzene-2,5-[poly(ethylene glycol) methyl ether]-1,4- bis(boronic acid ethanediol ester) (**6**).



Scheme 1.2. Synthesis of benzenebis(boronic ester) comonomer with amphiphilic poly(ethylene glycol) methyl ether side chains as solubilizing groups.

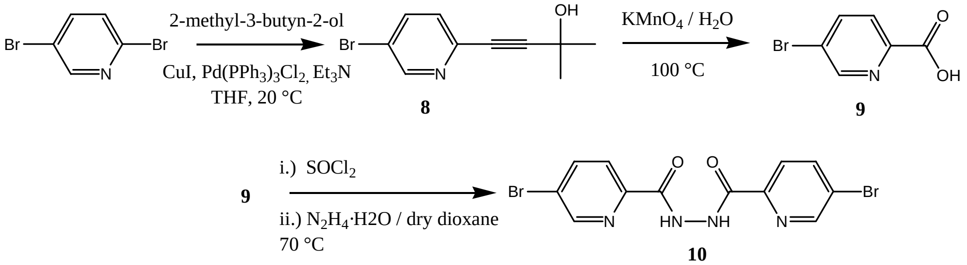
The two comonomers are then polymerized using a metal-mediated coupling reaction, which is shown in Scheme 1.4. Compounds **2** and **6** are dissolved in degassed tetrahydrofuran and an aqueous sodium bicarbonate solution, also degassed. The solvents are degassed under argon in order to remove oxygen that may poison the metal catalyst. The metal catalyst, palladium(0) tetrakis(triphenylphosphine), is dissolved in degassed THF and then added to the reaction mixture.



Scheme 1.3. Synthesis of **Polymer I** via palladium-catalyzed coupling polymerization.

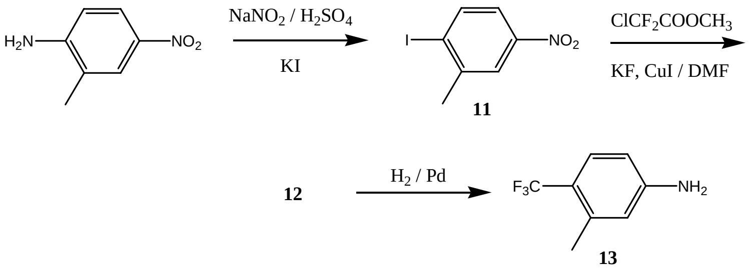
III. B. Polymer II Synthesis

Polymer II, begins with 2,5-dibromopyridine. In Scheme 2.1, an alkyne, 2-methyl-3-butyn-2-ol, is added using copper iodide, bis(triphenylphosphine)palladium(II) chloride, and triethylamine in tetrahydrofuran, yielding 4-(2-bromo-5-pyridyl)-2-methyl-3-butyn-2-ol (**8**). The alkyne is oxidized to a carboxylic acid using potassium permanganate in water, forming 5-bromopyridine-2-carboxylic acid (**9**). The acid is converted to the acid chloride using thionyl chloride, and then reacted with hydrazine monohydrate in dry dioxane to produce N,N'-bis(5-bromopyridine-2-carbonyl) hydrazide (**10**).[9]



Scheme 2.1. Synthesis of N,N'-bis(5-bromopyridine-2-carbonyl) hydrazide.

The synthesis of the amine from which the triazole is formed is shown in Scheme 2.2. 4-Iodo-3-methylnitrobenzene (**11**), is formed via diazotization of 2-methyl-4-nitroaniline and addition of potassium iodide. Compound **11** is trifluoromethylated using methyl chlorodifluoroacetate, potassium fluoride, and copper iodide in N,N-dimethylformamide, producing 3-methyl-4-trifluoromethylnitrobenzene (**12**). After reduction with palladium and hydrogen gas, 3-methyl-4-trifluoromethylaniline (**13**) is produced.[10]



Scheme 2.2. Synthesis of 3-methyl-4-trifluoromethylaniline.

13 is first converted to its phenylphosphazonanilide analog (see Figure 6) *in situ* using phosphorus trichloride in *o*-dichlorobenzene, and then adding **10** to form 3-(5-bromopyridinyl)-4-(3-methyl-4-trifluoromethylphenyl-5-(5-bromopyridinyl)-1,2,4-triazole (**14**),[11] as shown in Scheme 2.3. In the subsequent step, the methyl is brominated using N-bromosuccinimide and a catalytic amount of benzoyl peroxide in carbon tetrachloride to form 3-(5-bromopyridinyl)-4-(3-bromomethyl-4-trifluoromethylphenyl-5-(5-bromopyridinyl)-1,2,4-triazole (**15**).

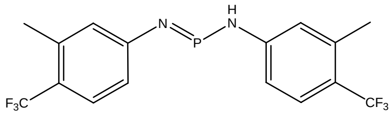
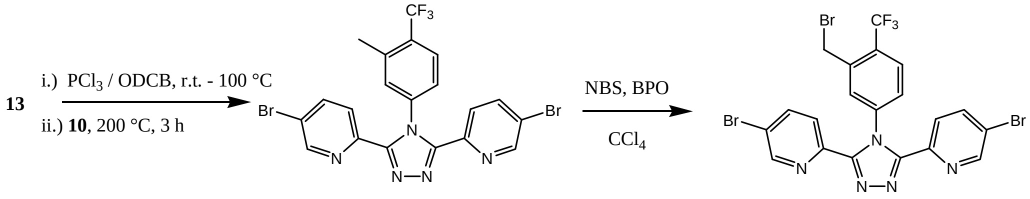


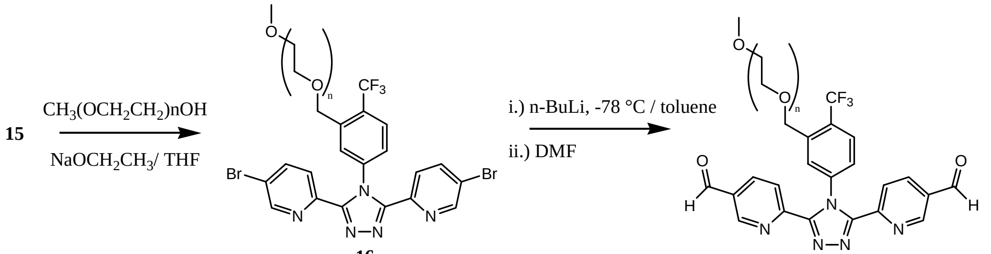
Figure 6. Phenylphosphazoanilide analog of 3-methyl-4-trifluoromethylaniline.



14 **15**

Scheme 2.3. Synthesis of 3-(5-bromopyridinyl)-4-(3-bromomethyl-4-trifluoromethylphenyl-5-(5-bromopyridinyl)-1,2,4-triazole.

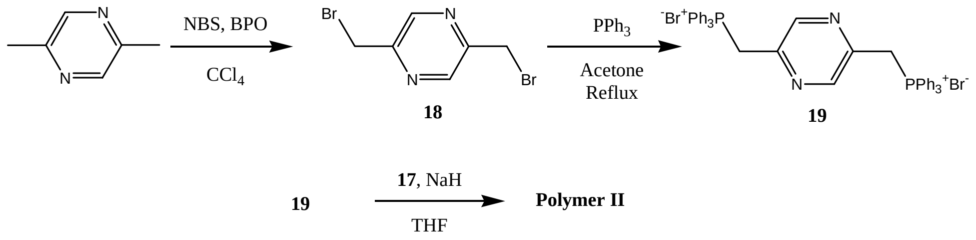
The synthesis of the triazole comonomer ends in Scheme 2.4 where the solubilizing group is connected by deprotonating poly(ethylene glycol) monomethyl ether with sodium ethoxide in tetrahydrofuran, followed by addition of **15** to form 3-(5-bromopyridinyl)-4-(3-[poly(ethylene glycol) methyl ether]methyl-4-trifluoromethylphenyl-5-(5-bromopyridinyl)-1,2,4-triazole (**16**). The bromines on the pyridine rings are then converted to aldehydes by using n-butyllithium in toluene, followed with addition of N,N-dimethylformamide, and a water work up yielding 3-(pyridinyl-5-carbaldehyde)-4-(3-[poly(ethylene glycol) methyl ether]methyl-4-trifluoromethylphenyl-5-(pyridinyl-5-carbaldehyde)-1,2,4-triazole (**17**).



16 **17**

Scheme 2.4. Synthesis of 3-(pyridinyl-5-carbaldehyde)-4-(3-poly(ethylene glycol) methyl ether methyl-4-trifluoromethylphenyl-5-(pyridinyl-5-carbaldehyde)-1,2,4- triazole.

Scheme 2.5 shows the syntheses of the pyrazine comonomer **19** and **Polymer II**. It begins with the bromination of 2,5-dimethylpyrazine using N-bromosuccinimide in carbon tetrachloride with a catalytic amount of benzoyl peroxide, generating 2,5-bis(bromomethyl)pyrazine (**18**). 2,5-bis(triphenylphosphonium bromide)pyrazine (**19**) is formed by refluxing **18** with triphenylphosphine in acetone. **Polymer II** is formed by the Wittig reaction between the bis(Wittig salt) **18** and the triazole dialdehyde **17**.



Scheme 2.5. Synthesis of 2,5-bis(triphenylphosphonium bromide)pyrazine and polymerization with the triazole dialdehyde via the Wittig reaction.

IV. Characterization

There are numerous techniques available to fully characterize the material's chemical structure, optical properties and physical properties. The structures of these materials can be determined by using proton and carbon NMR spectroscopy, FT-IR spectroscopy, and mass spectrometry. The optical properties can be determined by UV/Vis/NIR absorbance and fluorescence/phosphorescence spectrophotometry. The thicknesses of films can be measured using a profilometer. The electronic properties can be evaluated via two methods: the first being room temperature dc conductivity using the four point probe technique of a electrometer and current source; and the second being cyclic voltammetry, with a potentiostat/galvanostat using a three electrode cell with platinum electrodes as the counter and working electrodes and a silver/silver ion used as a reference electrode.

V. Summary

The syntheses of two electron deficient conjugated polymers are proposed using efficient reactions from commercially available chemicals. Both polymers include electron deficient imino-heterocycles, which should provide good electron mobilities. Poly(ethylene glycol) methyl ether groups serve as amphiphilic solubilizing groups on both polymers, and should provide solubility in both organic and aqueous solvents. Quantum chemical calculations predict similar band gap energies for both polymers and that the degree of twisting between the rings along the polymer backbone may not be enough to disrupt the conjugation of the systems.

VI. References

---

[1] Thelakkat, M.; Schmidt, H.-W., *Polym. Advan. Technol.*, **1998**, *9*, 429.

[2] Baum, P.; Meyer, W. H.; Wegner, G., *Polymer*, **2000**, *41*, 965.

[3] *Gaussian 03, Revision B.04*, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M., Scalmani, G., Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-

---

Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A., *Gaussian, Inc., Pittsburgh PA,* **2003**.

[4] Aleman, C.; Julia, L., *J. Phys. Chem.*, **1996**, *100*, 1524.

[5] Claudio, G. C.; Bittner, E. R., *Chem. Phys.*, **2002**, *276*, 81.

[6] Brédas, J. L.; Street, G. B.; Thémans, B.; André, J. M., *J. Chem. Phys.*, **1985**, *83*, 1323.

[7] Peng, Z.; Galvin, M. E., *Chem. Mater.*, **1998**, *10*, 1785.

[8] Cianga, I.; Hepuzer, Y.; Yagci, Y., *Macromol. Symp.*, **2002**, *183*, 145.

[9] Wang, C.; Kilitziraki, M.; Palsson, L.-O.; Bryce, M. R.; Monkman, A. P.; Samuel, I. D. W., *Adv. Funct. Mater.*, **2001**, *11*, 47.

[10] Kuo, E. A.; Hambleton, P. T.; Kay, D. P.; Evans, P. L.; Matharu, S. S.; Little, E.; McDowall, N.; Jones, C. B.; Hedgecock, C. J. R.; Yea, C. M.; Chan, A. W. E.; Hairsine, P. W.; Ager, I. R.; Tully, W. R.; Williamson, R. A.; Westwood, R., *J. Med. Chem.*, **1996**, *39*, 4608.

[11] Klingsberg, E., *J. Org. Chem.*, **1958**, *23*, 1086.