Developing synthetic strategies and studying potential applications of buckybowl corannulene polymers

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**Developing Synthetic Strategies and Studying Potential
Applications of Buckybowl Corannulene Polymers**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2020

Developing Synthetic Strategies and Studying Potential Applications of Buckybowl Corannulene Polymers

Zhang Zhuang

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

A thesis submitted to the Nanyang Technological University in partial fulfilment of the requirement for the degree of Doctor of Philosophy

2020

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The contributions of the co-authors are as follows:

- Prof Stuparu provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts.
- I co-designed the study with Prof Stuparu and performed all the laboratory work. I also analyzed the data.
- All microscopy, including sample preparation, was conducted by me.

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Abstract

The bowl-shaped polycyclic aromatic ($C_{20}H_{10}$) hydrocarbon, corannulene, constitutes a recognizable motif on the curved surface of buckminsterfullerene (C_{60}). Therefore, the scientific community has heavily investigated it for its structure and properties. One aspect that is still relatively less studied is its application in the arena of macromolecular science. In the past 50 years of corannulene chemistry, only a few synthetic examples are known in this context. Therefore, the aim of this thesis is to examine corannulene derivatives as polymerization initiators and monomers to access novel polymers and study their properties and applications. In this regard, the first chapter of this thesis introduces the reader with the literature so far on polymers of corannulene. In the second chapter synthesis of corannulene is described. In the third chapter, preparation of corannulene-based polymerization initiator is discussed and linear polymers are synthesized successfully using atom transfer free radical polymerization method. In the fourth chapter, corannulene is used as a monomer in palladium-catalyzed Stille polycondensation process to access network geometry. The morphology of these polymers was investigated and finally they were applied in supercapacitor devices. This work indicated that corannulene polymers are potential active materials for electrochemical energy storage and the devices show good stabilities and long recyclability. In essence, this thesis work enhances the repertoire of corannulene polymers and shows their applicability in real life devices.

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Chapter 1

Introduction to Buckybowl Corannulene and its Application in Polymer Science

In this chapter, the non-planar structure of corannulene and properties arising from it are discussed that make it different than planar polycyclic aromatic hydrocarbons. This discussion is followed by literature examples in which corannulene is used as a central motif in the preparation of polymers.

1. Structure of Corannulene

Curved aromatic compounds such as fullerene and carbon nanotubes have been receiving great attention from the materials science community for the past quarter of a century. This interest is primarily due to their extraordinary electronic properties.¹⁻⁴ Corannulene ($C_{20}H_{10}$) can be imagined as the cap region of fullerene C_{60} that exhibits molecular curvature due to the arrangement of five six-membered rings around a central five-membered ring (Figure 1).⁵⁻¹¹ Due to this structural resemblance with fullerene C_{60} , corannulene is also touted to be a useful building block in the construction of functional soft materials.

Figure 1. Chemical structures of carbon nanotube, fullerene C_{60} , and corannulene.

The common motif is the curvature of the molecular structure.

Initially, it remained unclear whether corannulene would adopt a bowl-like structure. 5-membered ring facilitate curvature and the central corannulene ring is a five membered ring. However, one would also think that going away from planarity would reduce aromaticity. Therefore, a planar structure would be preferred. It is in

1976 that the first crystal data confirmed the molecularly curved structure of corannulene with a bowl-depth of 0.87 Å.¹²

2. Properties of Corannulene

The nonplanarity of the structure imparts corannulene with unique properties that are not found in planar aromatic compounds such as anthracene or pyrene and are discussed below.

2.1. Dipole Moment

A consequence of adopting a curved conformation is the formation of a significant dipole moment (2.1 D).¹³ This arises from different electronic distribution on the concave and convex surfaces of corannulene resulting from differences in orbital overlap on either surface. Such a high dipole moment is not found in organic molecular materials similar in their molecular weight to corannulene.

2.2. Electron Affinity

Being a fragment of fullerene C₆₀, corannulene retains the molecular curvature and displays similar properties. For example, like C₆₀, which can accept 6 electrons, corannulene is also electron deficient and can accept up to 4 electrons.¹⁴ Its electron affinity and thus ability to be reduced is demonstrated by its tetraanionic form in the presence of Li. The Li⁺ ions intercalate between two eclipsed corannulene tetraanionic “decks” (Figure 2).¹⁵ Planar and flat aromatic compounds such as pyrene and anthracene are, on the other hand, electron rich. In comparison to C₆₀, however, corannulene is not as good an electron acceptor. Fortunately, corannulene has much

higher solubility in common organic solvents and therefore it can be derivatized easily to enhance its electron affinity. A general approach here is to introduce electron deficient groups on the periphery of corannulene. This includes trifluoromethyl¹⁶ and sulfone groups.¹⁷ In some cases, the electron affinity can be increased so much that it reaches the reduction potential of fullerene derivatives.

Figure 2. Tetraanionic double deck of corannulene with five intercalated lithium cations.

2.3. Complexation with C₆₀

Due to fewer five-membered rings in the molecular structure, corannulene is comparatively relaxed than fullerene C₆₀. Therefore, its convex structure wraps perfectly around the concave surface of C₆₀ (Figure 3). Besides a geometric fit, the resulting complex structure is stabilized by aromatic stacking interactions of the two molecules. This is the basis for design of many hosts based on the chemistry of corannulene to capture C₆₀ as a guest molecule. Such strategies are often useful in purification of C₆₀ from carbon soot. Interestingly, however, the complex between pristine corannulene and C₆₀ is not stable enough in solution. Therefore, either two corannulenes should be attached together to create a tighter cavity and enhance the

favourable stacking interactions or multivalency of polymeric structure is used to create stable complexes. For example, a corannulene dimer can bond to fullerene C₆₀ with high binding constant ($K_{\text{assoc}} = 8600 \pm 500 \text{ M}^{-1}$) (Figure 3).¹⁸

Figure 3. X-ray crystal structure of a corannulene receptor with fullerene C₆₀.

2.4. Dynamic Inversion of the Bowl

Being curved on a molecular level also brings something special to corannulene. It can flip its bowl at room temperature (Figure 4). This bowl-to-bowl inversion of corannulene proceeds via a planar transitions state, in a similar manner to ammonia. It is possible to study this dynamic process through variable temperature NMR of substituted corannulene such as dimethylcarbinol corannulene.¹⁹ Due to this substituent, diastereotopic protons could be observed by ¹H NMR. At room temperature these protons appear as a single peak, whereas at 183 K they gave distinct singlets. Therefore, the temperature of peak coalescence can be used to calculate the barrier to inversion to be about $10.2 \pm 0.2 \text{ kcal mol}^{-1}$ at 209 K.

Figure 4. Bowl-inversion of corannulene that is known to go through a planar transition state.

2.5. Host-Guest Interactions

This area of research investigates hosting of corannulene in guest molecules having a cavity. For example, it is shown that gamma cyclodextrin, the largest cyclic oligosaccharide, is capable of forming a 1:1 complex with corannulene through hydrophobic interactions in water.²⁰ This finding was later used to form ultrasmall nanoparticles by mixing corannulene with gamma cyclodextrin in a microfluidic chamber.²¹ Due to corannulene these particles were emissive. And due to cyclodextrin these particles were biocompatible (Figure 5).

Figure 5. A cartoon depicting docking of corannulene into the hydrophobic cavity of cyclodextrin. Normally such complexation is driven by solvophobic interactions.

A very recent study showed that corannulene can be hosted in the cavity of a tetracationic cyclophane (Figure 6).²² The purpose of this study was to examine the energy barrier for the bowl-to-bowl inversion of unsubstituted corannulene. The results confirmed the earlier studies using dimethylcarbinol substituted corannulene in ^1H NMR spectroscopy.

It is clear that this area of research is in its infancy and that corannulene polymers may provide a new building block in construction of supramolecular materials.

Figure 6. Chemical structure of the cyclophane (left) and crystal structure of its complex with corannulene (right).

3. Potential for Polymer Synthesis

In contrast to C_{60} , however, corannulene offers high solubility in common organic solvents and an avenue for multiple and well-defined substitutions on the aromatic scaffold. These two attributes are important to the synthetic polymer chemist as they allow for synthesis of monomers and polymerization initiators, and synthesis, purification, and unequivocal structural characterization of the resulting polymeric materials.

Scheme 1 shows some of the possible pathways to polymers beginning with corannulene halides as key components. Corannulene halides can be accessed in a

very practical manner (see Chapter 2 for details). For example, bromocorannulene and dimethyldibromocorannulene both can be synthesized by a simple bromination reaction of corannulene or dimethylcorannulene. Bromocorannulene can then be subjected to a Kumada coupling protocol to install a hydroxyl group. Such group can undergo an esterification reaction to give an acrylate monomer. Alternatively, the hydroxyl group can already be employed as an initiator for ring opening polymerization. If electronically conjugated polymers are required then corannulene halides can be used directly along with corannulene acetylenes or boronic esters. The acetylenes and boronic esters can be installed from the halide precursors. In this way, either Sonogashira-Hagihara protocol or Suzuki reaction catalysed by palladium catalysts can be used to access polymers in which the corannulene units can have delocalization of π electrons. By simply switching the nature of the monomer, the polymer architecture can be governed. For example, if there are two reactive sites on the corannulene nucleus then linear polymers come into being. If more than two active sites are placed on the corannulene then it act as a crosslinking point thus giving rise to crosslinked networks.

Scheme 1. Corannulene halides, acetylenes, and boronic esters are key components in design of a number of architecturally and electronically different polymers.

Therefore, taking advantage of unique properties of corannulene and its well-defined derivatization chemistry, a large effort now is focused on preparation of polymeric structures based on corannulene. In this regard, in the next section, we will discuss the literature examples that employ corannulene as a building block for polymer synthesis.

4. Corannulene in Polymers

The idea of combining corannulene chemistry with polymer science was first presented in 2011.²³ In this article, various synthetic routes were identified. This included pathways to dendritic architectures, linear polymers of single stranded and double stranded nature, and star polymers. Since this, a number of research groups have joined this growing area of research and various strategies presented in the aforementioned article have been successfully realized. In the following few pages we will review these activities in details.

In 2013, a new class of fullerene C_{60} hosts based on the corannulene motif was introduced through a careful design of the molecular structure of the polymer repeat unit and the mode of interaction between the repeat unit and the C_{60} molecule (Figure 7).²⁴ These hosts were prepared through a free radical polymerization process. The authors showed that the designed receptor-monomer, corannulene acrylate, could be readily converted into polymer hosts of various chemical compositions. Additionally, the interaction between the polymers and the fullerene C_{60} could be fine-tuned by modulating the chemical structure of the polymer repeat unit, chemical nature of the solvent, and temperature. A general nature of this design was then demonstrated by preparing an amphiphilic block copolymer that was capable of transporting C_{60} molecules into water. It should be mentioned that C_{60} is hydrophobic in nature and therefore insoluble in water. However, once the block copolymer is part of the solution then it forms a micellar structure and hosts C_{60} in its core through favorable interactions with corannulene.

In this manner small pockets of C₆₀ could be stabilized in water. The C₆₀/polymer composite materials could also be isolated as powders or freestanding films.

Figure 7. Synthesis of corannulene side-chain polymers (top), their interaction with fullerene C₆₀ through a ball-and-socket type of aromatic stacking interactions (middle), and bulk materials before and after supramolecular complexation (bottom). The digital picture of NMR tubes show solutions of corannulene polymer (top), C₆₀ (bottom), and corannulene polymer+C₆₀ in deuterated chlorobenzene (middle).

A follow-up study then changed the molecular design of the polymers through using corannulene as a polymerization initiator to access corannulene-core star-

shaped polymers (Figure 8).²⁵ Both, ring opening polymerization and atom transfer radical polymerization were shown to be applicable in the present design. The final polymers interacted with fullerene C₆₀ through their cores as opposed to the side chains of the aforementioned polymers. In this case, the interaction strength between the polymer host and the C₆₀ guest could be modulated through a combination of the solvent and the chemical nature of the polymeric arms.

Figure 8. Synthesis of corannulene-core star polymers through ring opening (top) and free radical polymerizations (bottom).

Recently, it was shown that if the polymeric arms were hydrophilic then the complete structure become amphiphilic due to hydrophobic nature of the corannulene core (Figure 9).²⁶⁻²⁷ Polyethylene glycols were used as arms and the polymer dissolves in water through favourable hydrogen bonding interactions

between water molecules and the oxygen atom of the polymer chains and aromatic stacking interactions of the core segments. However, upon heating, an entropy-driven dehydration process occurs and the clear solution becomes turbid. The turbid solution was investigated to be composed up of long fibrillar structures with enhanced emission. Finally, the thermal transition point could be modulated within the range of 30-50 °C by changing the length of the polymeric arm.

Figure 9. Thermoresponsive corannulene-core star polymers. Top shows the chemical structures while bottom left is an SEM image of the assembled fibres and right is the visual inspection of the aqueous solution with increasing temperature from left to right frames.

In a completely different molecular design than discussed so far, corannulene and bis-thiophene were combined in a polymer backbone by Lu *et al.* (Figure 10).²⁸

The synthesis here was based upon Stille coupling. For this corannulene-based dibromide was used as an AA monomer and bis-thiophene di-tin compound was used as the corresponding BB type of monomer. The palladium catalyzed Stille coupling reaction then gave rise to the electronically conjugated linear polymer chains. Due to electron donating nature of bis-thiophene and electron poor nature of corannulene, the polymer represented a donor/acceptor type of structure and was successfully applied in field-effect transistors.

Figure 10. Donor/acceptor polymer alternating the corannulene with thiophenes in the backbone structure.

Discrete oligomers of defined length and number of repeating units through use of an acetylene-based π -bridge between corannulene and thiophene were then reported by Li *et al.* (Figure 11).²⁹ The continuity of the electronic interaction is found to be good in the first three oligomers ($n = 0, 1, 2$) of the series. In the last two soluble oligomers ($n = 2, 3$) this property weakened. This may be due to a loss in planarity of overall molecule at longer lengths ($n = 3$). For the first time in this study, corannulene chromophores were shown to be active for non-linear optical activity (Figure 12). In this regard, longer oligomers ($n = 1, 2$) were shown to have a large two-photon absorption cross-section as well as two-photon-excited bright

luminescence. Until this point, corannulene derivatives were not known to possess such two-photon absorbance and emission activities.

Figure 11. The concept of planar-nonplanar discrete oligomers carrying corannulene and thiophene segments.

Figure 12. Digital picture showing an 800 nm laser passing through the chloroform solution of the oligomers.

Going away from linear and completely organic polymers, Fellows *et al.* presented an impressive new design of organic/inorganic hybrid and non-linear structure. They created metal-organic frameworks as a new type of coordination polymer based on corannulene. In this design, metal (Zn^{2+}) ions are coordinated to corannulene ligands through carboxylic acid groups thus creating a 3-dimensional porous structure with channels of $9 \times 13 \text{ \AA}$ size (Figure 13).³⁰ These coordination polymers showed emission and redox activity due to the presence of corannulene but better than pristine corannulene nucleus. This work constituted the first example of a 3-dimensional corannulene polymer with electroactive porous structure.

Figure 13. Metal organic frameworks with corannulene as a 3-dimensional coordination polymer with porosity and electroactive behaviour. The top shows the tetraphenylcorannulene with tetraacid groups used for the coordination purposes with zinc cations.

Smaldone and coworkers further pushed knowledge in this area of porous polymers through preparation of fully organic structure that can be better in its stability to metal organic frame works. Yet, such porous polymers will still have large surface area comparable to metal organic frameworks (Figure 14).³¹ The synthesis here is based on metal-catalyzed Sonogashira-Hagihara cross coupling reaction between corannulene bromides and phenylene ethynynes. The resulting polymeric networks were amorphous lacking distinct π - π stacking interactions between aromatic units. Just like metal organic frameworks described above, Smaldone's organic porous polymers were also electroactive due to the presence of the corannulene segment. More importantly, however, these materials were capable of CO₂ and H₂ storage. This really indicates a future applicability of corannulene polymers in gas storage applications.

Figure 14. Preparation of network polymers through palladium catalyzed Sonogashira-Hagihara reaction. B2/B3/B4 denotes alkyne monomers with the

number of alkyne functionalities. The tetrabromide corannulene monomer is designated with A4 showing four reactive sites. A and B shows monomer types.

Just like insolubility of Smaldone's crosslinked polymers, Mishra *et al.* used ring-opening metathesis to synthesise insoluble corannulene nanomaterials through a ring opening metathesis precipitation polymerization process using a ruthenium catalyst (Figure 15).³² The insolubility originated from the hydrocarbon structure of the repeating unit and its strong self-aggregation through aromatic stacking interactions and not by chemical crosslinking. The aggregates showed diameters of 400-980 nm and with an average pore size of 1.4 nm. Application in supercapacitor devices showed that the corannulene polymers were useful in storing energy through a pseudocapacitive charge storage mechanism. Although a number of carbon-rich materials can be used for this purpose. However, the corannulene nanomaterials showed a very long-term stability through charge and discharge cycles. For instance, the devices showed 90% capacitance retention even after undergoing 10,000 cycles. This was the first example that showed a real life device application of corannulene polymers.

Figure 15. Synthesis of corannulene nanoparticles by ring opening metathesis polymerization (top). SEM image of the nanomaterials (left bottom) and digital picture of the bulk material (top right).

5. Conclusions

To summarize, corannulene is a bowl-shaped aromatic hydrocarbon that bears structural similarities with fullerene C_{60} . For example, corannulene is electron deficient. However, being an open structure, the bowl can flip and the molecule has bowl-inversion dynamics. Due to two electronic faces of the bowl, the molecule has high dipole moment. It can recognize fullerene C_{60} through a ball-and-socket type of stacking interaction. It can also be hosted by other guest molecules such as cyclodextrins or cyclophanes. With all these properties, it is an enticing idea to make polymers from this building block. This field, however, is in its infancy and only a handful of examples can be found so far. These examples are very encouraging as the resulting polymeric materials exhibit interesting properties and some of them are applicable in real-life devices. Therefore, an overall goal of this thesis work is to

increase the range of corannulene polymers and study the properties of the newly designed materials.

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Chapter 2

Synthesis of Corannulene

In this chapter, historical approaches in the synthesis of corannulene are presented along with the most recent breakthroughs. Finally, synthesis and characterization carried out during this thesis work are presented.

1. Introduction

In 1966, Barth and Lawton showed that corannulene could be prepared in a 17-step synthesis.¹ The overall yield was <1%. They utilized acenaphthene **1** as the starting material and the strategy was such that the introduction of molecular strain was avoided until the final stages of the synthesis (**2**) (Scheme 1). Although this was a ground breaking synthesis but the very many steps and an overall low yield did not permit its wide applicability.

Scheme 1. Corannulene synthesis by Lawton and Barth.

Following this, the field of corannulene remained dormant for a quarter of a century until Larry Scott published a novel route to this beautiful molecule.² Not only it was a new way of preparing curved aromatics the method was also efficient and practical. This method is called 'flash vacuum pyrolysis' (FVP). Here, high temperatures (800-1200 °C) are applied in the gas phase to overcome energy barriers required to introduce molecular curvature. Conversion of substrate to the product depends upon the reaction time and temperature. Through this method, Scott's group prepared corannulene in only three linear synthetic steps and in an

overall yield of 26% (Scheme 2). Briefly, in an optimized FVP pathway to corannulene, acenaphthenequinone **4** was used as the starting materials to give 7,10-bis(1-chloroethynyl)fluoranthene **5** in two steps. Compound **5** then served as the pyrolysis precursor to afford **1**.

Scheme 2. Flash vacuum pyrolysis synthesis of corannulene developed by Scott's group (FVP temperature = 1100 °C)

Later, several other FVP-based synthetic routes were developed.³⁻⁸ In this, we can recognize routes in which the central ring comes into being as a result of pyrolysis such as in structures **6-9** (Scheme 2). The second approach is in which a five membered ring is already part of the precursor structure (**10-15**).

Scheme 2. FVP precursors that lead to corannulene upon pyrolysis.

The FVP syntheses opened the way to study the many interesting properties of the molecule as discussed in the introduction. However, FVP suffers from low selectivity, which results in by-product formation. It is also not tolerant of functional groups. Therefore, mild solution-phase syntheses methods were still required and were developed later to the FVP work.

The first (improved) solution phase synthesis was by Siegel and coworkers in which brominated derivative **16** of fluorene gave access to a tetrahydrodimethylcorannulene **17** (Scheme 3).⁹ The molecule could be aromatized by using DDQ in 18% yield through dehydrogenation process. This synthesis was

further improved by Siegel himself¹⁰ by producing octabromo derivative under forcing conditions and then subjecting it to the treatment of low valent vanadium or titanium to obtain corannulene.

Scheme 3. Second solution-phase synthesis by Siegel.

Independent work from Sygula and Rabideau further improved practicality of the synthesis as they showed that metal catalysts were not required and the tetrabromide **18** could be converted into tetrabromocorannulene **19** with the help of sodium hydroxide (Scheme 4).¹¹ The tetrabromide can be used as is or it can be debrominated to give bare corannulene. In these improved protocols, a final aromatization step was not needed.

Scheme 4. Sygula and Rabideau's synthesis of corannulene.

In 2012, Siegel's group further optimised the solution phase process in a manner that the amounts of solvents, reagents, time, and the number of

chromatographic purifications were considerably reduced. The optimized procedure used chloroxylene **20** as the starting material, which provides corannulene in an overall yield of 8.7%. In this way large amounts of corannulene (in kilogram scale) can now be prepared in a cost effective and efficient manner (Scheme 5).¹²

Scheme 5. Large-scale solution-phase synthesis of corannulene developed by Siegel's group.

2. Results and Discussion

Towards achieving goal of this thesis, a large amount of corannulene was required so that functionalization aspects and polymerization aspects could be studied.

Therefore, corannulene was prepared on a multigram scale from the diketone precursor as is shown in Siegel's kilogram scale synthesis discussed above. The diketone itself was obtained from a commercial supplier.

The synthesis therefore required a five-step synthesis (Scheme 6-10). In the first two steps, the aldol condensation of **23** with 3-pentanone and subsequent retro-Diels-Alder addition furnished 1,6,7,10-tetramethylfluoranthene (**24**). **24** is subjected to a benzylic radical bromination reaction under photochemical irradiation to obtain 1,6,7,10-tetrakis-(bromomethyl)fluoranthene (**25**). Sodium hydroxide deprotonated the remaining benzylic hydrogen and initiated carbon-carbon bond formation, forming tetrabromocorannulene (**26**). Tetrabromocorannulene is useful as a monomer itself as is shown in Chapter 4 of this thesis and can be used at this stage. However, to obtain bare corannulene a last step is to remove the bromine atoms through the help of palladium on charcoal.

Scheme 6. Synthesis of **27**.

Scheme 7. Synthesis of **24**.

Scheme 8. Synthesis of **25**.

Scheme 9. Synthesis of **26**.

Scheme 10. Synthesis of **3**.

In terms of purification, the first step does not require any purification and **27** can be taken to the next step as prepared. After the next step, however, a chromatographic purification is necessary. The next two steps do not require any purification and the products can simply be washed and taken to the next step. The final reaction that yields corannulene, however, requires column chromatography for purification. In this manner, only two steps require chromatographic purification and add to the practicality of synthesis.

3. Experimental Details

Synthesis of **27**: To a stirred solution of KOH (294 g, 5.231 mol, 22 equiv.) in MeOH (770 mL) was added 3-pentanone (164.25 g, 1.902 mol, $d = 0.815$ g/L, 201.5 mL, 8 equiv.) at rt. Then dione **23** (50 g, 0.237 mol) was added to the reaction mixture portion wise and brown solution was stirred at 18-25 °C for 2 h. Then reaction mixture was cooled to 0 °C and acidified between P^H 5 to 7 by previously cooled 50% con. HCl solution (1:1 of con. HCl:H₂O, $\approx$ 600 mL). Then suspension was stirred for 20 mins, filtered, washed with H₂O and then dried under vacuum to afford compound **27** (66.8 g) and the obtained intermediate was used for next step without further purification. ¹H NMR (500 MHz, CDCl₃): δ 2.87 (s, 6H), 7.49 (d, 2H, $J = 8.28$ Hz), 8.03 (d, 2H, $J = 8.28$ Hz); ¹³C NMR (100 MHz, CDCl₃): δ 18.12, 76.58, 77.00, 77.42, 124.29, 127.47, 130.63, 131.73, 137.57, 147.10, 188.80.

Synthesis of **24**: The dried compound **27** (66.8 g) was dissolved in Ac₂O (585 mL, $d = 1.08$ g/L, 26 equiv.) and norbornadiene (194 mL, $d = 0.906$ g/L, 8 equiv.), and

refluxed at 130-140 °C for 3 days under N₂ atmosphere. Then reaction mixture was brought to rt and volatiles were evaporated at 80 °C (300 mbar), and Ac₂O and NBD was recovered and stored. Water (20 mL) was added to crude to quench trace amount of Ac₂O and evaporated. Then solid residue was cooled to rt, MeOH (100 mL) was added to precipitate and refluxed for 30-45 mins on water bath of Rotary evaporator). Then stirred overnight at rt, suspension was filtered, washed with H₂O (400 mL) and finally dried under vacuum to afford crude tetramethyl compound **24** (72 g). The obtained crude was purified by SiO₂ column chromatography using hexane as an eluent to afford pure compound **24** (40 g, 0.155 moles, yield 65%). ¹H NMR (500 MHz, CDCl₃): δ 2.74 (s, 6H), 2.84 (s, 6H), 7.13 (s, 2H), 7.35 (d, 2H, *J* = 8.28), 7.67 (d, 2H, *J* = 8.28); ¹³C NMR (100 MHz, CDCl₃): δ 24.30, 25.13, 126.15, 126.60, 129.63, 130.67, 131.83, 132.00, 133.67, 134.88, 139.91.

Synthesis of **25**: To a stirred solution of tetramethyl compound **24** (19.0 g, 73.54 mmol) in chlorobenzene (427 mL) was added AIBN (192 mg, 1.169 mmol, 0.016 equiv.) and NBS (153.3 g, 861 mmol, 11.7 equiv.) at 75 °C while illuminating 300 W bulb, then 400 mbar vacuum was applied and reaction mixture was heated at 90-95 °C. After 3 h and 9 h AIBN (192 mg) was added in two portions and continued to stir up to 24 h. Then reaction mixture was cooled to 40 °C and suspension was filtered. The filtrate was evaporated at 70 °C (120 mbar) and distillate was used to wash filter cake. After evaporation of solvent, residue was dissolved in EtOAc (100 mL) and heated at 70 °C for 20 mins, then cooled to 20 °C, stirred overnight and suspension was filtered under vacuum, washed with EtOAc (60 mL) and finally dried under vacuum to afford compound **25** (49 g, 55.08 mmol, yield 75%). ¹H NMR (500 MHz,

CDCl₃): δ 7.10 (s, 2H), 7.22 (s, 2H), 7.99 (d, J = 8.5 Hz, 2H), 8.22 (s, 2H), 8.28 (d, J = 8.5 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 38.5, 39.0, 127.6, 130.1, 130.2, 131.5, 131.8, 132.3, 136.5, 137.9.

Synthesis of **26**: To a stirred solution of compound **25** (43.7 g, 49.15 mmol) in *i*-PrOH (440 mL) was added 30 wt% NaOH solution (62.36 g, 467.9 mmol, 9.52 equiv.) at 80-85 °C for the period of 45 mins. After completion of the addition, the reaction mixture was stirred for additional 1.5 h and then slowly brought to rt. The reaction mixture was filtered using sintered glass funnel, washed with H₂O (100 mL), *i*-PrOH (60 mL) and dried overnight under vacuum to afford compound **26** (22.5 g, 39.76 mmol, yield 81%). ¹H NMR (400 MHz, CDCl₃): δ 7.98 (s, 2H), 7.95 (d, J = 8.9 Hz), 7.85 (d, J = 8.9 Hz, 2H).

Synthesis of **3**: To a stirred solution of compound **26** (22.5 g, 39.76 mmol), formic acid (17.38 g, d = 1.22 g/L, 14.24 mL, 377 mmol, 9.5 equiv.) and Et₃N (38.78 g, d = 0.725 g/L, 53.49 mL, 383 mmol, 9.64 equiv.) in 3-picoline (298 mL) was added 10% Pd-C (50% H₂O, 909 mg). The suspension was heated to reflux ($\approx$ 140 °C) for 16 h and then reaction mixture was brought to rt, filtered to remove ammonium formate, washed with 3-picoline (300 mL) and then volatiles were evaporated to give solid residue and this was purified on SiO₂ column using hexane as an eluent to afford pure corannulene **3** (9.0 g, 35.94 mmol, yield = 90%). ¹H NMR (500 MHz, CDCl₃): δ 7.82 (s, 10H). ¹³C NMR (100 MHz, CDCl₃): δ 127.2, 130.8, 135.8.

4. Conclusions

In the past half-century since the first synthesis of corannulene was reported, the synthetic protocol have been improved immensely. First FVP came on the scene and a number of corannulene properties could be studied. Then, second solution-phase synthesis from Siegel was presented and improved by him and independently by Sygula and Rabideau. Very recently, Siegel developed a kilogram scale synthesis. Now, therefore, the community has access to this interesting polycyclic aromatic hydrocarbon in a very efficient manner. For this thesis work, five step synthesis from diketone obtained from a commercial supplier is carried out to access corannulene. In these five steps only two steps require chromatographic separation and the rest of the synthetic step require only washing of the crude product. The overall yield for the five step ranges from X-X%. Having access to corannulene the work for the next chapter was designed and carried out.

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Chapter 3

Synthesis of Corannulene End-Chain Polymers

In this chapter, design and synthesis of new polymerization initiators based on the corannulene structure is discussed. Subsequently, atom transfer radical polymerization of styrene and methylmethacrylate monomers is carried out using these initiators. The resulting polymers were then investigated for their interaction capabilities with fullerene C₆₀.

1. Introduction

In context of corannulene and polymers, one particular strategy that has not been explored so far is the preparation of polymers bearing one corannulene unit as the polymer chain-end. It can be envisaged that such polymers can associate through either aromatic interactions for example if fullerene C₆₀ is added to the polymer solution. The aim of this chapter is therefore to primarily explore if polymerization initiators can be synthesized having one active site through controlled polymerization protocols such as atom transfer radical polymerization process.

1.1. Atom Transfer Radical Polymerization (ATRP)

Atom Transfer Radical Polymerization (ATRP) is one type of Controlled Radical Polymerization (CRP) processes, and it is considered as one of the most powerful and versatile method within CRP.¹ The most outstanding advantage of ATRP is the precise control over molecular weight distribution (MWD), molecular weight (M_w), molecular architecture and functionality. Furthermore, ATRP can be conducted in a variety of different solvents even including water, and relative mild conditions such as room temperature. It is also suitable for modified the molecular structure with most functional groups.² By tuning the polymerization conditions and reaction parameters, the reaction kinetics can be easily controlled. In addition to traditional solution polymerization including homogeneous and heterogeneous polymerization, ATRP also provide a novel strategy to construct polymers grown on various

substrates, such as the surfaces of organic or inorganic materials including nanoparticles (NPs), and even proteins.³⁻⁵

1.2. ATRP in Polymer Architecture and Functionality

ATRP has been already successfully used in synthesizing various copolymers with originally any desired complex polymer architecture with controlled topology. The most direct way of ATRP is to synthesize linear chain polymers with exactly controlled dispersity and dimensions. Besides that, ATRP is also widely used in preparing various branched structures such as the copolymers of macromonomers, copolymers formed using inimers, difunctional and multifunctional initiators, grafted polymers on functional backbones, and even cyclic structures.

ATRP was not only used in periodic and gradient systems, but also in preparing segmented (block and graft) copolymers and precisely control chain composition. ATRP is tolerant of many functional groups, which makes it can also be used in incorporate functionalities after polymerization.⁶⁻⁷ Therefore, ATRP can be used to synthesize polymers which have different functional groups placed in different positions. It is including the polymers with one functional group, two groups and even more groups with the same or different functionalities. It also can be as a macromonomer which is polymerizable. This method can be even extended to prepare multifunctional polymers, such as star polymers and brush polymers which have relative regular structure, and hyperbranched polymers with a less regular structure.⁸⁻¹¹

1.3. Conduct an ATRP

ATRP can be conducted in multitudinous methods, including bulk polymerization, solution polymerization, and heterogenous media polymerization, in which a variety of media such as suspension, dispersion, emulsion, microemulsion, miniemulsion and inverse miniemulsion can be used. The primary key to choose the media is the solubility issues and heat transfer properties. The selected conditions should make sure that the catalyst complex, the reactant and the product is at least partially soluble in the reaction medium. For example, for the polymerization of acrylonitrile a solvent is required to dissolve the product, since the polymer is not soluble in the monomer and the solvent can avoid vitrification at high conversion when the polymerization of a high Tg polymer conducts at room temperature.¹²

Copper based catalysts have been developed as the most commonly used catalyst for an ATRP, since the relative activity of the copper catalyst complexes cover a range of seven orders of magnitude. It is obvious that based on the monomer and the set of conditions the ligand must be chosen carefully to form a suitable catalyst complex to conduct the polymerization.

To appropriately select the catalyst for ATRP, it is very important to understand thoroughly the concurrent electron transfer reactions which impact the performance of catalyst. One simple example is disproportionation. Besides that the most pronounced in Cu-mediated ATRP and the redox of carbon radicals, which includes reduction of radicals to carbanions and oxidation to carbocations, should also be paid more attention. Furthermore, the radical coordination to the metal catalyst can result in interactions between CRP mechanisms.

1.4. Mechanism of ATRP

Scheme 1. Mechanism of ATRA and ATRP conducted by transition metal catalyst. (R-X, alkyl halide; -X, halide group; $R^\cdot$, radical; Mt^z , metal ion in oxidation state z; L, ligand; Y (i and ii), side group of ATRP monomer)¹

As shown in Scheme 1, ATRP depends on building an equilibrium between initiating species such as alkyl halide or pseudohalide, R-X, and radicals. The radicals are created through the cleavage of the C-X bond by activator Mt^zL_m , which is a redox-active, low-oxidation-state metal complex, where Mt^z stands for the metal atom or

ion in oxidation state z and L is a ligand. In the first activation stage, which is characterized by the rate constant k_{act} , the activator Mt^zL_m is oxidized to high-oxidation-state and coordinated with a (pseudo) halide ligand to form the deactivator $X-Mt^{z+1}L_m$. And the deactivator $X-Mt^{z+1}L_m$ is capable to quickly transfer the atom or group X back to the radicals, making them into dormant alkyl (pseudo) halides. This process is called as deactivation relayed on k_{deact} . When the initially yielded radicals reacted with a monomer, it will afford $P_n\cdot$, a polymeric radical (n stands for the degree of polymerization, DP), and the deactivation will yield alkyl halide oligomers or polymers which are designated as P_n-X .

From a viewpoint of mechanism, ATRP is in fact a type of atom transfer radical addition ATRA. Both ATRP and ATRA are relevant to radical addition reaction of alkyl halides throughout an unsaturated C–C bond. Compared with ATRA, in ATRP the unsaturated compound in which the alkyl halide adduct is reactivated, is the monomer. And the reaction of the formed radical with additional monomer molecules makes the polymer propagation. Activation and deactivation processes occur during the whole polymerization. In order to precisely control the ATRP procedure, the deactivation should be sufficiently fast. It can make sure that not too many monomer units are added to the propagating polymeric radicals throughout each stage of activity.³

2. Design of Corannulene Initiators

One derivative of corannulene that can easily be prepared is corannulene aldehyde (**1**) (Scheme 2). The chemistry used is Rieche formylation and the isolated yields are

quantitative. The aldehyde group in **1** can be reduced to produce a benzylic alcohol **2**. The benzylic alcohol can be subjected to a bromination reaction with the help of PBr₃ to give benzyl bromide initiator **3**. Alternatively, the hydroxyl group can be subjected to an esterification reaction to give initiator **4**. Both, **3** and **4** are active under the ATRP mechanism discussed above.

Scheme 2. Synthesis of corannulene-based polymerization initiators.

3. Experimental Details

1: To a vacuum dried round bottom flask containing dry CH₂Cl₂ (100 mL) solution of corannulene (2.0 g, 8.0 mmol, 1 eq) and dichloromethyl methyl ether (3.7 g, 31.8

mmol, 4 eq) was added a solution of TiCl_4 (1.75 mL, 31.8 mmol, 4 eq) in CH_2Cl_2 (15 mL) dropwise at 0°C under N_2 atmosphere, and the mixture was stirred for 1 h at 0°C and then for 20 h at room temperature. After completion of reaction, the reaction mixture was poured into ice-water and extracted with CH_2Cl_2 (3×100 mL). The combined organic layer was washed with saturated NaCl, dried over anhydrous Na_2SO_4 and concentrated under vacuum. The resulting yellow solid was washed with hexane to afford 2.11g of corannulene aldehyde **1** (yield = 95 %). Yellow solid; R_f = 0.50 (hexane/ethyl acetate = 4:1); mp = 198–200 $^\circ\text{C}$; δ (400 MHz, CDCl_3) 10.33 (1 H, s), 8.60 (1 H, d, J 8.9), 8.26 (1 H, s), 8.00 – 7.67 (7 H, m). δ_c (101 MHz, CDCl_3) 193.29, 139.16, 138.09, 136.51, 135.97, 135.19, 135.10, 134.90, 132.39, 131.16, 130.84, 128.88, 128.79, 128.70, 127.79, 127.68, 127.58, 127.35, 127.24, 127.09, 127.05, 127.04. HRMS (m/z) [$M + H$] $^+$ calcd for $\text{C}_{21}\text{H}_{11}\text{O}$: 279.0810; found: 279.0823.

2: To a solution of corannulene aldehyde (0.5 g, 1.79 mmol, 1 eq) in THF/MeOH (1:3 mL) mixture was added NaBH_4 (0.34 g, 8.96 mmol, 5 eq) under N_2 atmosphere. The reaction mixture was stirred for 1.5 h at room temperature. After completion of reaction, the reaction mixture was quenched with water and extracted with CH_2Cl_2 (3×50mL). The combined organic layers was washed with saturated NaCl, dried over anhydrous Na_2SO_4 and concentrated under vacuum. The resulting crude was purified by silica gel column chromatography (hexanes/ ethyl acetate) to afford corannulene methanol as a yellow solid (490 mg) in 97% yield. Yellow solid; R_f = 0.20 (hexane/ethyl acetate = 4:1); mp = 152–154 $^\circ\text{C}$; δ (400 MHz, CDCl_3) 7.99 (1 H, d, J 8.9), 7.82 – 7.71 (8 H, m), 5.20 (2 H, s). δ_c (101 MHz, CDCl_3) 139.25, 136.21, 136.07, 135.78, 135.74, 130.93, 130.92, 130.74, 130.70, 129.56, 127.40, 127.33, 127.30,

127.18, 127.17, 127.06, 127.00, 125.31, 124.95, 63.82. HRMS (m/z) [M + H]⁺ calcd for C₂₁H₁₃O: 281.0966; found: 281.0961.

Initiator 3: To an ice-cold solution of corannulene methanol (250 mg, 0.891 mmol) and pyridine (0.072 mL, 0.891 mmol) in 30 mL of dry THF, was added phosphorus tribromide (0.169 mL, 0.891 mmol) and the resulting solution was stirred for 12 h. The reaction mixture was neutralized with saturated sodium bicarbonate solution. The organic layer was separated, and the solvent was evaporated under reduced pressure. The resulting crude was purified by silica gel column chromatography to afford corannulene methyl bromide as a colorless solid (230 mg) in 73% yield. Colorless solid; *R*_f = 0.65(hexane/ethyl acetate = 4:1); mp = 206–207 °C; δ_H (400 MHz, CDCl₃) 8.06 (1 H, d, *J* 8.8), 7.89 (1 H, d, *J* 8.8), 7.84 – 7.72 (7 H, m), 5.07 (2 H, s). δ_C (101 MHz, CDCl₃) 136.23, 136.21, 136.04, 135.83, 135.79, 135.76, 131.30, 131.06, 130.93, 130.57, 129.28, 127.97, 127.57, 127.55, 127.31, 127.21, 126.92, 124.66, 31.39. HRMS (m/z) [M + H]⁺ calcd for C₂₁H₁₂Br: 343.0122; found: 343.0096.

Initiator 4: To an ice-cold solution of corannulenylmethanol (300 mg, 1.070 mmol) in dry DCM (30 mL), was added Et₃N (119.1 mg, 1.177 mmol) and propanoyl bromide (270.6 mg, 1.177 mmol), and the resulting mixture was stirred for 2 h. The reaction mixture was neutralized with saturated aqueous sodium hydrogen carbonate solution. The organic layer was separated, and the solvent was evaporated under reduced pressure. The resulting crude product was purified by silica gel column chromatography to afford initiator 4 in 81% yield. δ_H (400 MHz, CDCl₃) 7.96 (1 H, d), 7.85 (1 H, t), 7.78 – 7.80 (7 H, m), 5.72 (2 H, s), 1.98 (6 H, s).

ATRP procedure: As shown in Scheme 3, by using brominated corannulene derivatives as initiator in ATRP, poly(methyl methacrylate) (PMMA) and polystyrene (PS) with corannulene unit at the end of polymer molecule were synthesized. Reaction conditions were optimized by testing various effects, such as temperature, reaction time, monomer concentration and so on.

A typical ATRP was conducted as followed by using PMMA as an example. Methyl methacrylate (2 g, 1 equiv.) was dissolved into 0-2 mL of anisole. Initiator (0.01 equiv.) was added followed by the addition of 0.015 equiv. of PMDETA and 0.01 equiv. of Cu(I)Br. The polymerization mixture was degassed, sealed under argon, and keep in 0-60 °C for 1-24 h. After this time, the polymerization vial was opened to air, cooled down to room temperature, and then precipitated into methanol. The solid was obtained by filtered, washed with MeOH, and dried. PMMA, δ_H (400 MHz, CDCl₃) 7.61 – 7.94 (9 H, m), 3.23 – 3.90 (91 H, m), 0.48 – 2.26 (391 H, m), about 30 repeat units. PS, δ_H (400 MHz, CDCl₃) 7.47 – 7.97 (9 H, m), 6.15 – 7.22 (330 H, m), 0.62 – 2.32 (375 H, m), about 66 repeat units.

4. Results and Discussion

Having access to initiators **3** and **4**, polystyrene (PS) and polymethyl methacrylate (PMMA) polymers were synthesized (Scheme 3).

Scheme 3. Synthesis of corannulene-end polymer.

4.1 Characterization

As shown in Figure 1, the corannulene-end PMMA and PS were successfully synthesized. For both PMMA and PS, the multiplet peaks from about 7.5 to 8.0 ppm indicated the existence of corannulene group in the polymer chain. In Figure 1a the two peak signal at 3.60 ppm and 1.81 ppm corresponds to the methoxy and methylene protons of PMMA main chain. Besides, the two signals around 0.85 ppm and 1.02 ppm are assigned to the methyl group. The absence of the peak signal at around 5.90 ppm and 5.40 ppm confirms that PMMA is pure without any unreacted MMA monomers. The ^1H NMR spectrum of PS in Figure 1b shows five resolved bands of the aromatic protons at 7.1-6.2 ppm which resulted from the overlapping

multiplets of the five spin system. The CH and CH₂ bands (2.2-1.0 ppm) are largely separated but individually are not resolved. That further proved these two corannulene derivatives can be used as initiator in ATRP.

Figure 1. NMR spectra (¹H NMR, CDCl₃) of corannulene-end (a) PMMA and (b) PS.

Table 1 shows the GPC results of all the PMMA samples gotten in various conditions. The solvent amount, temperature, reaction time and initiator type show some effects on the molecular weight and DPI of PMMA. Compared with bulk

polymerization, adding anisole as solvent induced larger molecular weight and larger DPI. Temperature shows the most important effect on M_n and DPI. With the temperature increasing, the DPI shows an obvious increment while M_n has small change. Meanwhile, reaction time shows less effects on M_n and DPI, unless it was lengthened to a long time (20 h).

Table 1. GPC results of corannulene-end PMMA under various conditions.

No.	anisole/M	T (°C)	t (h)	M_n	M_w	M_w/M_n
1	0	r.t.	3	12700	19600	1.55
2	0.25	r.t.	3	12900	26100	2.02
3	0.5	r.t.	3	27700	119300	4.31
4	0	-7	1	17800	27900	1.57
5	0	-7	2	19100	28000	1.47
6	0	0	1	21700	41000	1.89
7	0	0	2	18600	27500	1.48
8	0	0	4	20700	39400	1.90
9	0	0	1	19300	29300	1.52
10	0	60	3	20800	75800	3.64
11	0	0	20	14300	47500	3.32
12*	0	r.t.	3	22300	39400	1.76
13*	0	60	3	22300	63300	2.84

* Sample 12 and 13 used initiator **2** as initiator, while others used initiator **3**.

Depending on the optimized conditions, another series of PMMA sample were prepared (Table 2). When the temperature is up to 90 °C, the M_n and DPI is sharply increased. It indicated that the temperature is a very important fact in PMMA polymerization. The effect of reaction time was confirmed by lengthening it to a very long time (96 h), compared with M_n , the increment of DPI is not obvious.

The GPC curves were showed in Figure 2. Sample PMMA 2 show the most uniform and symmetrical peak, which indicated the lowest DPI in all PMMA samples. Other

samples' curves are a little asymmetric, even contained some shoulder peaks, which caused by the high DPI.

Table 2. GPC results of corannulene-end PMMA under optimized conditions.

No.	M:I	T (°C)	t (h)	M_n	M_w	M_w/M_n
1	10000	25	24	-	-	-
2	5000	25	24	21100	28600	1.35
3	2500	25	24	30400	59900	1.97
4	5000	60	24	23600	53700	2.27
5	5000	90	24	51400	182300	3.55
6	5000	25	96	44600	91500	2.08

Figure 2. GPC curves of corannulene-end PMMA.

Compared with PMMA, as shown in Table 3, PS with lower DPI which reach about 1.08 can be obtained under convenient conditions. That may be caused by the more similar chemical structure of styrene monomer and corannulene derivative initiator.

Table 3. GPC results of corannulene-end PS under various conditions.

No.	aniso/M	T (°C)	t (h)	M_n	M_w	M_w/M_n
1	0	r.t.	16	2000	2400	1.20
2	0	60	16	8000	8600	1.08
3	0	90	16	125300	244100	1.95

Same as the PMMA, depending on the optimized conditions, another series of PS sample were prepared (Table 4). Temperature is also the most important factor on the reaction. It shows an obvious increment of M_n when the temperature increases, while the DPI shows almost no change. However, compared with the reaction of PMMA, both reaction time and the ratio of monomer and initiator show less effect on the ATRP reaction. The GPC curves of PS were shown in Figure 3. All the curves show uniform, symmetrical and sharp peak, which indicated the low DPI.

Table 4. GPC results of corannulene-end PS under optimized conditions.

No.	M:I	T (°C)	t (h)	M_n	M_w	M_w/M_n
1	10000	60	24	22700	25200	1.11
2	5000	60	24	14300	16100	1.12
3	2500	60	24	20800	23000	1.11
4	5000	25	24	-	-	-
5	5000	60	96	17500	20900	1.20
6	5000	80	24	51900	66300	1.28
7	5000	90	24	90100	117100	1.30

Figure 3. GPC curves of corannulene-end PS.

4.2. Low VT NMR Investigation

Low VT NMR was used to investigate the interaction between these polymers and C_{60} . As shown in Figure 4, the peak at 143 ppm belongs to the internal standard C_{60} , and the peak with higher chemical shift belongs to the C_{60} added into PMMA solution. The chemical shift of the C_{60} peak increased by the decrease of temperature. That means at lower temperature the interaction between C_{60} and the polymer was stronger. The corannulene group can be seen as a holder of C_{60} molecule in this system.

Figure 4. ^{13}C NMR (400 MHz, $\text{C}_6\text{D}_5\text{Cl}$) of corannulene-end PMMA and C_{60} complex under variety of temperatures.

Low VT NMR was also used to investigate the interaction between these PS and C_{60} . As shown in Figure 5, different from PMMA, there were no chemical shift of the C_{60} peaks under different temperature. This may be because in the PS polymer the corannulene group was covered inside the styrene chain, where the C_{60} can not reach. It confirmed that the interaction between C_{60} and polymer was mainly caused by the corannulene group.

Figure 5. ^{13}C NMR (400 MHz, $\text{C}_6\text{D}_5\text{Cl}$) of corannulene-end PS and C_{60} complex under variety of temperatures. (No IS indicates the sample without internal standard C_{60} at 20 °C.)

5. Conclusions

In conclusion, a series of corannulene end-chain PMMA and PS were successfully synthesized via ATRP. The reaction conditions, including the solvent amount, temperature, reaction time and the ratio of monomer and initiator, were discussed. After the optimization, PMMA and PS with lowest DPI were obtained and were used in the investigation of the interaction of C_{60} and corannulene group. The low VT NMR showed that there is an interaction between corannulene group and C_{60} molecule in the PMMA system but not in PS system.

6. References

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Chapter 4

Synthesis of Properties of Polymeric Corannulene Networks

In this chapter, molecular design for accessing non-linear network-type polymers using tin-based Stille coupling reaction is described. Furthermore, application of these polymers for electrochemical energy storage in supercapacitor devices is discussed.

1. Introduction

Conjugated polymers have attracted much academic and industrial interests as organic semiconducting materials, because of their potential applications on electronic and optoelectronic devices, such as organic solar cells (OSCs), organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), electrochromic devices and so on. They offer more opportunities to resolve energy-related issues, and are also considered as advanced materials of display and information technological devices. Compared with traditional inorganic semiconducting materials, conjugated polymers have obvious advantages including their low cost, light weight, good flexibility and especially convenience to be processed, which provides possibilities for large-scale fabrication of electronic or optoelectronic devices.¹⁻⁴

More recently, many researchers have been particularly attracted by a unique member of conjugated polymers, which named donor-acceptor (D-A) polymers.⁵ D-A polymers integrate electron donors and electron acceptors with an alternating array in one polymer molecule. Their intramolecular donor-acceptor interactions can lower the band gap, which is an important property of electronic and optoelectronic materials. Furthermore, the intramolecular and intermolecular interactions between donor and acceptor moieties can lead to more ordered structures and enhance the stacking of polymer chains. Therefore, in recently researches, D-A polymers are favored in design of various electronic and optoelectronic devices including field-

effect transistors,⁶⁻⁷ electrochromic devices,⁸ light-emitting diodes,¹⁰⁻¹¹ solar cells¹²⁻¹³ and other related materials.¹⁴⁻¹⁵

Figure 1. Effect of orbital couplings of donor and acceptor units to the bandgap.¹⁶

1.1. D-A polymer Structure

As the name suggests, D-A polymers are composed of two parts, donors and acceptors. Donors are electron-rich moieties, while acceptors are electron-poor moieties. The electron pushing or pulling ability, the interactions between them and the molecular geometry determine the basic electronic properties of D-A polymer. In the view of molecular orbitals, in D-A polymer molecule, the donor moieties mainly occupy the HOMO, and the acceptor moieties mainly occupy the LUMO (Figure 1), thus both HOMO and LUMO energy levels and hence bandgaps can be well tuned conveniently by changing the structures of donors or acceptors.

Figure 2. Typical (a) donors and (b) accepters.

Donors refer to electron-rich moieties which determine the HOMO energy level of D-A polymer molecules. Most of reported donor moieties are derived from benzene and thiophene. As shown in Figure 2a, there are a great number of

combination constructed of these two basic units. According to the presence of the bridging atoms, and the formation of thiophene-benzene fused units, donor moieties derived from benzene and thiophene can be classified into two types.

Acceptors refer to electron-poor moieties which determine the LUMO energy level of D-A polymer. Most acceptors have at least one or more strong electron-poor groups, like imine nitrogen (C=N) or carboxyl group (C=O). As shown in Figure 2b, they can be sorted into five types by their chemical structure, including thiadiazole-, thiazole-, imide-, pyrazine-, and carboxyl-containing acceptors.

1.2. Design Strategy

The fundamental design of new D-A polymer is not only the design of novel donors and acceptors, but also the alteration of them incorporated into polymers. The modification in design will affect the band gap and hence the properties directly. Furthermore, when they are fabricated to functional devices, the design also affects the backbone geometry, molecular interaction, packing orientation, and microstructure, which have great influences on the efficiency of electronic or optoelectronic devices. This section will discuss the most widely used design strategies and their effects on the properties of D-A polymer.

Backbone chain is the basic skeleton of polymer, and has great effects on polymer's properties. Janssen and co-workers researched the effects of different donors moieties made up of thiophene, benzene, or fused aromatics in the backbone chain of diketopyrrolopyrrole (DPP)-based D-A polymers. The solubility of the different backbone units showed obvious effects on the fibril microstructure of

polymer (Figure 3a). A series of semicrystalline fibril with different widths showed a clear linear correlation between the fibril widths and the external quantum efficiencies (EQE) for photon to electron conversion (Figure 3b). The EQE and power conversion efficiencies can reach as high as 60% and 7.1% respectively when the fibril widths were less than 12 nm.¹⁷

Figure 3. (a) Fibril with different width fabricated by polymers with various backbone; (b) the correlation between the widths of the fibrils and the external quantum efficiencies (EQE).¹⁷

The group of Briseno and Russell also reported a backbone engineering about the fibrillar network morphology and orientation for DPP-based polymers. They used fluorine-thiophene, terthiophene, or quaterthiophene as donors. By slightly changing the chemical structure of donors, the fibril orientation and size change markedly. And the fibril orientation strongly influenced the transport properties when used in OFETs. Furthermore, these fibril structures were also influenced by the processing conditions.¹⁸

The team led by Park, Kim and Kwon reported a novel D-A polymer contained selenophene units as donors replaced the traditional thiophene donors. The vinyl bonds linked adjacent selenophene units can extend the conjugation length, consequently enhanced intermolecular interactions. The obtained D-A polymer showed an obviously high carrier mobility of $4.97 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which caused by the more mobile lone pair of selenophene atoms. Furthermore, this D-A polymer showed a highly ordered structure.⁷

In addition to the traditional D-A type polymers, Qin, Müllen, Watkins and co-workers presented a unique D-A polymer with A-D1-A-D2 repeating units. This novel polymer could control of the supramolecular interactions including both the regiochemistry of backbone and the amount of nonchromophoric components.

In addition to backbone engineering, side-chain engineering also plays an important part in the design of function enhanced D-A polymers. Tuning the side-chain group is a directly strategy to design various D-A polymer with different band gap. Azoulay, Bazan, and co-workers used an imine substituent as the bridgehead group of cyclopentadithiophene (CPDT), to synthesize a series of corresponding D-A polymers with different side-chain group. The HOMO-LUMO energy levels of these D-A polymers can be fine-tuned (Figure 4).¹⁹

Figure 4. The tuned HOMO-LUMO energy levels via side-chain engineering.²⁰

Yang, Oh, and co-workers reported on the side-chain engineering of a DPP-based D-A polymer. They used diketopyrrolopyrrole-selenophene copolymers with hybrid siloxane-solubilizing groups to enhance ambipolar performance in OFETs, which can be systematically tuned by the side-chain alkyl spacer length. By attaching siloxane-solubilizing groups, unprecedentedly high charge carrier mobilities of $8.84 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for holes and $4.34 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for electrons can be gained respectively.²¹

Another side-chain engineering example of DPP-based D-A polymer is reported by Fréchet, Chen, and colleagues. They used either linear or branched alkyl side-chain with different length to control the properties of DPP-based polymers containing furan in backbone applied as OFET. The type of side-chain group showed obvious effects on the solubility, crystallinity, packing, and in-plane orientation of the π -stacking. The OFET fabricated of the liner ones displayed higher charge carrier mobilities.⁶

Both the backbone engineering and the side-chain engineering are essential for the successful design of D-A polymers. They should not be isolated, but flexibly used in combination. Hou, Wu and co-workers reported a step-by-step design approach of

D-A polymer applied on polymer solar cells (PSCs). Firstly, strong electron-poor groups were applied to the backbone, and the HOMO of polymers was effectively lowered. And then, the LUMO was tuned by side-chain group. Using this method, they gained PSCs with increased open-circuit voltage as well as high short-circuit current density, which finally resulted in a PSC with a high power conversion efficiency of 6.77%.²²

When fabricating devices, D-A polymers are usually used as films. At that time, the film morphologies and the interaction between polymer molecules plays an increasing important part in the electronic and optoelectronic properties. Depending on different chemical structure of D-A polymer, the strategies to enhance the packing are different and complex.

The general view is that polymers with centrosymmetric units induce better packing and crystallinity because they are more easily to obtain better π - π stacking. As Figure 5 shown, for the D-A polymers with centrosymmetric donors, the “smaller units” and “larger units” can array as a stagger way. In the films the linear backbone which parallel to the substrate is lead to better lamellar packing.²³

Figure 5. D-A polymers with different symmetries and their film packing (a) with centrosymmetric and (b) with axisymmetric donors.²³

Durrant, Heeney, and co-workers found a ladder-type fused ring donor, dithienogermolodithiophene, can improve the packing and molecular interactions by increasing the planarity of D-A polymers, thus achieve a higher performance of OSCs with an optical band gap of 1.75 eV and efficiency of 7.2%. This donor was consisted of two thienothiophene units bridged by a dialkyl germylene unit.¹²

Wang, Li, Yu, Li, and colleagues reported a naphthodithiophene-based D-A polymers, which contained “zigzag” electron-rich donors. The special shape of donors was thought to induce stronger π -stacking by facilitating π -electron delocalization, thus enhanced efficient charge transport.²⁴

There are no absolute rules for D-A polymer design. Marks, Facchetti, and co-workers developed a good packing dialkoxybithiazole-based D-A polymer with head-to-head linkages, which should traditionally be avoided because of the poor π - π stacking and amorphous film microstructures induced by backbone torsion. They

ensured the high backbone planarity resulting in an extended π -conjugation while lowering the HOMO and band gap.²⁵

Chemical structure is not the only influence factor of D-A polymer packing. The groups of Facchetti and Neher reported a type of naphthalenediimide-based D-A polymer. They used different solvents to prepare thin films in order to tune the degree of aggregation. The types of solvents showed a dramatic impact on the packing. Different orientation of the polymer chains including edge-on and face-on microstructures were obtained and displayed distinct different performances.²⁶

The donor-accepter concept has already been successfully applied to low molecular weight oligomers, which can be seen as a short part of D-A polymers. Compared with polymers, oligomers show the unique advantages in terms of degree of crystallinity, purification, and distribution of molecular weight. Researches about the D-A oligomers have important meaning in guiding the design of D-A polymer.²⁷

Computational model system is also a powerful tool in researching D-A polymers to gain a deeper understanding. Friend and colleagues studied the intrachain charge generation and separation by model system. They observed a localized charge transfer state, which will significantly influence the interfacial electronic properties, which is very useful in design solar cells.²⁸

As a summary, the unique flexible donor-accepter structure endows D-A polymer with great potentials in enhancing their performances. It provides various design strategy and endless possibilities to improve their properties. The enormous potential for industrial applications in organic electronic and optoelectronic devices inspires the interests of researchers. Recently lots of research groups report the

design of novel D-A polymers with enhanced performance of electronic and optoelectronic materials, which opens the way to new energy material and information technology. However, to improve the industrial application of D-A polymers, there are still some challenges, such as further enhancement of the mobilities, the molecular packing control, and reproducibility and stability of the devices, which require the collective efforts and persistent exploration of scientists.

Corannulene, a nonplanar polycyclic aromatic hydrocarbon, which can be considered as a fragment of fullerene, consists of a cyclopentane ring fused with five benzene rings. Its bowl-shaped aromatic system displays different properties from the planar π -conjugated analogs. In recent years, it has attracted significant academic and industrial interest due to their potential applications in electronic and optoelectronic devices, such as organic solar cells (OSCs), organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and so on. In some recent researches, corannulene and its derivatives have been regarded as building blocks for polymers, especially π -conjugated polymers. Compared with inorganic materials and small molecule organic materials, polymers provide their unique advantages including light weight, low cost, good flexibility, and more convenience to be processed. Due to its electron-withdrawing ability, corannulene and its derivatives can be used as electron acceptor units in a donor-accepter system. That provides a possible strategy to design novel donor-accepter polymer. Furthermore, because the bowl shape of corannulene can give rise to strong interactions with fullerenes, corannulene and its derivatives can be used as hosts for fullerenes, including in polymeric architectures. This property provides an attractive method to prepare

carbon nano materials/polymer composites, which is an effective way to enhance the performance of polymers or the inorganic fillers. However unfortunately the corresponding research on the above mentioned two strategies is still very rare to date. Therefore, we plan to design a series of corannulene-based D-A polymers and use them as C₆₀ encapsulant, investigate the correlation between properties and structural characterization, and finally develop several electronic or optoelectronic devices with enhanced performance.

2. Experimental details

The synthesis strategy of crosslinked corannulene-*alt*-thiophene copolymers is shown in Figure6. 1,2,5,6-tetrabromocorannulene (monomer A) and the ditrialkyltin compounds (monomer Bn) were synthesized as previously reported protocols.²⁹⁻³⁰

Monomer Bn. Monomer B1 is used as an example, the other monomer Bn were synthesized by same procedure. *n*-BuLi (5.5 mL of a 1.6 M solution in hexane, 8.8 mmol) was added dropwise to a solution of 2,5-dibromothiophene (0.97 g, 4.0 mmol) in THF (25 mL) at -78 °C with stirring. After stirring for 1.5 h at -78 °C, trimethyltin chloride (9.2 mL of a 1.0 M solution in hexane, 9.2 mmol) was added slowly. The reaction mixture was stirred at -78 °C for additional 0.5 h, then gradually warmed to room temperature and stirred overnight. The mixture was poured into ice/water (50 mL), and the product was extracted with ether. The organic layer was washed twice with water, dried over Na₂SO₄, and then decolorized with charcoal. The solvent was removed by rotary evaporation. And final product was obtain by silica column (hexane).

The crosslinked polymers PABn were prepared via Stille coupling reaction. Monomer A and monomer Bn (mol. ratio 1:2) were added into anisole after nitrogen bubbling for 20 min. After adding a catalytic amount (5% mol) of $\text{Pd(PPh}_3)_4$, the polymerization was carried out at 110 °C for 3 days. Then after cooling down, the mixture was filtered to obtain black precipitation as product, which was washed by dichloromethane and acetone three times each to remove the tin compound.

Figure 6. Synthesis of corannulene-based network copolymers. (The dashed line indicates continuity of the polymeric structure.)

The morphology of the samples were analyzed using a field emission scanning electron microscope (FESEM; Zeiss) attached with an energy dispersive spectroscope. Fourier transform infrared spectroscopy (FTIR) was carried out using a Shimadzu IR Prestige Spectrometer.

The electrochemical tests were conducted in a three-electrode electrochemical cell with a Pt wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode, in 1 M Na₂SO₄ aqueous solution with the aid of a BioLogic SP-200 electrochemical workstation. The cyclic voltammetry was conducted with a voltage window of 0–1 V (vs. SCE) at different scan rates, while the galvanostatic charge–discharge tests were performed under various current rates. Electrochemical impedance spectroscopy (EIS) was carried out after charging at the open-circuit potential with a superimposed 5 mV sinusoidal (root-mean-square) perturbation over the frequency range from 100 kHz to 0.01 Hz.

3. Results and discussion

In order to use the donor-acceptor concept, electron rich thiophene, phenyl, and bi-phenyl di-tin systems were used as BB-type of monomers in conjunction with tetrabromocorannulene as an A4 monomer in a palladium-catalyzed step growth polymerization process (Figure 6). All the polymers is insoluble in common organic solvents indicating the formation of a crosslinked polymeric structure. The SEM images of samples PAB1, PAB2, PAB3, PAB4 and PAB5 are shown as Figure 7(a-e) respectively. It is obviously that the various morphology caused by difference monomer Bn. For PAB1, PAB2, and PAB3, which all contain thiophene group, it

seems that the more alkyl groups make more aggregation. Compared with the amorphous PAB1 (Figure 7a), PAB2 shows a tendency to grow up to bigger blocks (Figure 7b). And PAB3, which have two hexyl groups in monomer B, formed regular nanorods structure (Figure 7c). Moreover, it is interesting that when using phenyl as monomer B (PAB4, Figure 7d), a fine long nanowire structure is obtained. But meanwhile PAB5, which contains larger conjugated structure, only shows an amorphous formation (Figure 7e). Fig 2f shows the EDX spectrum of PAB1. The existence of Br element indicates that there are some drawbacks in the polymer caused by unreacted -Br group of monomer A.

Figure 7. SEM images of (a) PAB1, (b) PAB2, (c) PAB3, (d) PAB4, (e) PAB5 and (f) EDX spectrum of PAB1.

FTIR spectrum confirms the polymerization (Figure 8). Compared with monomer A, PAB1, PAB2 and PAB3 display a peak at about 700 cm^{-1} corresponded to thiophene C-S stretching vibrations. And PAB4 and PAB5 also show a signal at about 700 cm^{-1} which may belong to the bend of aromatic ring. And for all PABn samples, two peaks at 1576 cm^{-1} and 1459 cm^{-1} generated after polymerization. These two

peaks belong to the vibration of C-C bond combined by the two monomer **A** and **Bn**, which also indicated the formation of polymeric structure.

Figure 8. FTIR spectrum of the polymer products PAB1, PAB2, PAB3, PAB4, PAB5 and monomer A.

The electrochemical performance of the polymers was tested by CV and the GCD experiments through a three-electrode system. Figure 9a shows the CV curves of PAB1, PAB2, PAB3, PAB4 and PAB5 in 1M Na₂SO₄ aqueous electrolyte at a scan rate of 10 mV s⁻¹. The CV curve of all these samples has no pair of redox peaks, which indicates typical double-layer capacitance characteristics, wherein the shape is normally close to an ideal rectangular shape. In a typical double-layer capacitance, the important characteristic is the electrical double layer, which formed at the interface between electrode and electrolyte with opposing polarity charge. One layer formed with electrons at the surface of the electrode, and another one formed with ions in the electrolyte. And these two layers are typically separated by a single layer of solvent molecules that adhere to the surface of the electrode and act like a

dielectric in a conventional capacitor. The amount of electric charge stored in double-layer capacitor usually depends on the applied voltage. The specific capacitance of the polymers can be calculated via the integrated area of CV curve, and the results are shown in Figure 9b (74.2, 47.7, 61.6, 59.4 and 50.3 F g⁻¹ respectively).

Figure 9. (a) CV curve of the polymer products PAB1, PAB2, PAB3, PAB4 and PAB5 in 1M Na₂SO₄ aqueous electrolyte at 0–1 V at 10 mV s⁻¹ scan rate. (b) The specific capacitance calculated by the CV curve.

A further study of the CV property for PAB1 was investigated. Figure 10a shows the CV curves of PAB1 scanning at a voltage sweeping rate of 10, 20, 40, 60, 80 and 100 mV s⁻¹, respectively. The effective interaction between the electrode and the ions decreases as the scan rate increases, and the shape of the CV curves become more deflected. But there is still no pair of redox peaks displayed, and the shape almost remains unchanged, which implies that the PAB1 has a good rate capability response and highly capacitive nature with good ion. It can be confirmed by the un conspicuous decrease of specific capacitance of PAB1 at various scanning rate

(Figure 10b). The CV at different voltage windows is also investigated (Figure 10c). A redox peak at 0.6-0.7 V is becoming obvious with the increase of voltage windows.

Galvanostatic charge-discharge (GCD) tests were performed to further evaluate the electrochemical performance at different current densities. Figure 10d shows the GCD curves of PAB1 at current densities from 2 and 10 A g⁻¹. Charge-discharge time decreases with increase in current density, showing that the redox reaction is a diffusion-controlled process, which means high current densities impose that the redox reaction in the polymer occurs rapidly which reduces the electrode efficiency. The specific capacitance is calculated as 58.2 and 18.8 F g⁻¹ at 2 and 10 A g⁻¹, respectively. Another important factor for the polymers is the cycle stability subjected to long-term charge–discharge cycles. As shown in Figure 10e, after 300 cycles, the specific capacitance retention keeps as high as 97.4%. Figure 10f shows the Nyquist plots for PAB1 at room temperature. The intercept on the real axis (Z') represents the equivalent series resistance (ESR) is 0.55 Ω , which includes the ionic resistance of the electrolyte, the intrinsic resistance of the active material, and current collector.

Figure 10. Electrochemical performances of PAB1 in a three-electrode system in 1M Na₂SO₄ aqueous electrolyte. (a) CV and (b) the specific capacitance at different scan rates, (c) different voltage windows at 10mV/s. (d) charge/discharge profiles at different current density, (e) charge/discharge stability efficiency at 2 A/g in 300 times recycles, and (f) EIS spectrum.

4. Conclusions

In summary, a series of crosslinked corannulene-*alt*-thiophene copolymers were successfully synthesized. And their electrochemical properties investigation shows

close to an ideal CV curve shape, low equivalent series resistance and good charge-discharge stability, although the specific capacitive is not very high. It shows potential in developing corannulene-based polymer applied on preparing supercapacitor.

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Chapter 5

General Conclusions and Future Directions

I. The conclusions that can be drawn from this thesis work are as follows.

1. The synthesis of corannulene is practical and reproducible. It can be carried out on a milligram or multigram scale. Its solubility is high in organic solvents that are typically used in an organic chemistry laboratory. It is due to this reason that working with corannulene is free of problems generally encountered in the broad area of polycyclic aromatic hydrocarbon chemistry.
2. There is another beneficial feature of corannulene chemistry. It can be functionalized in a precise fashion. As seen in the third chapter it can mono-functionalized. As seen in the fourth chapter it can be tetra-functionalized. This allows for changing the macromolecular architecture. Mono-functionalization help in synthesis of linear architectures and tetra-functionalizations give rise to a network geometry.
3. Linear polymers having corannulene chain-end can be prepared by atom transfer radical polymerization process. Here, corannulene-base well-defined polymerization initiators can be synthesized and corannulene nucleus does not interfere with the radical polymerization process.
4. Tetrabromocorannulene can be combined with tin-based aromatic monomers in an A4/B2 type of palladium-catalyzed Stille polycondensation protocol. The generated networks bear corannulene as the electrochemically

active unit suitable for supercapacitor devices. The morphology of the material depends upon the nature of the B2 monomer. The devices show high stability and chemical reversibility processes.

II. The future directions can be identified as follows.

1. The corannulene chain-end polymers are so far prepared as a PMMA or PS homopolymer. Since atom transfer radical polymerization is applicable, one can use the controlled nature of this process to make block copolymers. For example amphiphilic structures can be accessed in which the corannulene gets the opportunity to be in the hydrophobic domains of micellar structures made by such amphiphilic structures in a favorable solvent for the second polymer block. Hence, guest molecules such as fullerene C_{60} can be encapsulated the micellar core. Host of fullerene C_{60} are technologically important and the present design may be utilized to create a new host family.
2. In terms of networks, it is great that they find applicability in the supercapacitor devices. Therefore, other chemistries should be explored for their synthesis. For example, a very good avenue is to replace the toxic tin compounds with borylated arene and use Suzuki polymerization to access the corannulene networks. Second, the corannulene scaffold can be substituted with amide or trifluoromethyl groups to further tune the reduction potential of the polymers. Such a study will shed light on the effect of substituent on the material and device properties and will help in enhancing the performance of the supercapacitors.

Abbreviations

ATRA	atom transfer radical addition
ATRP	atom transfer radical polymerization
CPDT	cyclopentadithiophene
CRP	controlled radical polymerization
D-A	donor-acceptor
DPP	diketopyrrolopyrrole
EIS	electrochemical impedance spectroscopy
EQE	external quantum efficiencies
ESR	equivalent series resistance
FESEM	field emission scanning electron microscope
FTIR	Fourier transform infrared spectroscopy
FVP	flash vacuum pyrolysis'
GCD	galvanostatic charge-discharge
M _w	molecular weight
MWD	molecular weight distribution
NPs	nanoparticles
OFETs	organic field-effect transistors
OLEDs	organic light-emitting diodes
OSCs	organic solar cells
PMMA	poly(methyl methacrylate)
PS	polystyrene

PSCs polymer solar cells

SCE saturated calomel electrode

Appendix

¹H NMR (CDCl₃) of corannulene

^1H NMR (CDCl_3) of Initiator **3** corannulene methyl bromide

^1H NMR (CDCl_3) of Initiator **4**

^1H NMR (CDCl_3) of 2,5-Bis(trimethylstannyl)thiophene

^{13}C NMR (CDCl_3) of 2,5-Bis(trimethylstannyl)thiophene

^1H NMR (CDCl_3) of 2,5-bis(trimethylstannyl)-3-hexylthiophene

^{13}C NMR (CDCl_3) of 2,5-bis(trimethylstannyl)-3-hexylthiophene

^1H NMR (CDCl_3) of 2,5-bis(trimethylstannyl)-3,4-dihexylthiophene

^{13}C NMR (CDCl₃) of 2,5-bis(trimethylstannyl)-3,4-dihexylthiophene

^1H NMR (CDCl₃) of 1,1'-(1,4-Phenylene)bis[1,1,1-trimethylstannane]

^{13}C NMR (CDCl₃) of 1,1'-(1,4-Phenylene)bis[1,1,1-trimethylstannane]

^1H NMR (CDCl₃) of 1,1'-(9H-Fluorene-2,7-diyl)bis[1,1,1-trimethylstannane]

¹³C NMR (CDCl₃) of 1,1'-(9H-Fluorene-2,7-diyl)bis[1,1,1-trimethylstannane]