PREPARATION OF FLAT DENDRIMERS AND POLYCYCLIC AROMATIC HYDROCARBONS CONNECTED VIA 1,3,5-TRIETHYNYLBENZENE CORE

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Flat dendrimers, consisting of a hexavalent aromatic core and rigid ethynyl units locked in place by ether connections were developed based upon the divergent synthetic method. Alternating functional groups were adopted on each site of the hexa-substituted benzene, in order to avoid undesired cyclization pathways. The flat structures of conjugated dendrimers would allow investigation on the discotic liquid crystal properties. In addition, these ethynyl dendrimers are expected to show directed energy and electron transfer with a highly conjugated system, and thus are effective in the preparation of photoreactive materials such as electronic sensors or light harvesting materials.

Conjugated polycyclic aromatic hydrocarbons, consisting of naphthalene, anthracene, pyrene, and phenanthrene groups connected via 1,3,5-triethynylbenzene cores, were synthesized. These molecules exhibited luminescence properties and the π-complexation with a mercury trifunctional lewis acid are expected to enhance the phosphorescence in the presence of the heavy metal due to the spin-orbit coupling. Besides, owing to the presence of heavy metal atom in the Au (I) complexes linked by σ-bonded triethynyltriphenylene luminophore, the phosphorescence occurs from a metal-centered emission. The conjugated organic luminophores have been developed to produce excellent quantum efficiencies, brightness, and long lifetimes.
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CHAPTER 1
INTRODUCTION TO DENDRIMERS

1.1 Background

Dendrimer chemistry has attracted increased interest and been a rapidly expanding area over the past two decades, with new classes emerging frequently since Vögtle and co-workers\(^1\) first introduced the structurally controlled synthesis of a dendrimer in 1978. The number of publications in the area, which involve the widespread potential of these highly branched macromolecules, has been increasing as well. Word dendrimer originated from Greek. It combines ‘\textit{dendron}’ meaning tree or branch and ‘\textit{meros}’ meaning part.\(^2\) Dendrimers are defined as 3-dimensional, highly branched, monodispersed macromolecules.

Dendrimers have some unique properties that differ from those of conventional linear polymer due to their dispersed globular shapes and many end-functional groups. Most linear polymers are generated by one-step polymerization resulting in a range of molecular species with broad molecular weight distributions and poorly defined molecular structures. On the other hand, dendrimers can be isolated and characterized as a single molecular weight compound because of the multi-step and complete reactions in the preparation of each generation layer, and the high symmetry of branching units. As opposed to linear polymers possessing only two end groups, dendrimers contain increased multifunctional end groups on the surface with gradual growth of generations. Therefore, the properties of dendrimers such as solubility, chemical reactivity and glass transition temperature depend on the characteristics of the end-functional groups as the structural size of dendrimers grows. In addition, unlike
linear polymers that can infinitely continue growth in the absence of solubility problems, dendrimer growth has physical limitations that the available volume with increased generations depends on the cube of dendrimer radius. Thus, dendrimers result in globular shapes of high generation structure, which shows higher molecular density from inside to outside.⁴

The structure of a dendrimer (Figure 1.1) can be divided into three zones: the region of the central core, the region of the inner branched repeat units emerging from this core and the outer level carrying the multifunctional end-groups. The encapsulated central core, that consists of multiple reaction sites with unique chemical properties can be surrounded by tailored branching units. The multivalent surface can adopt a lot of functionalities with a closely-packed structure that results in unique macroscopic properties.¹ As shown below (Figure 1.1), the typical dendrimer is spherical in nature resembling the shape of a round ball.

**Figure 1.1.** Structure of dendrimers.
1.2 The Construction of Dendrimers

Well-defined dendrimers can be generated in a series of stepwise and repetitive reactions from synthetic branched monomer units, which radiate from a core molecule. This synthetic approach allows the completion of each generation in the outer level. Furthermore, the synthetic design can control the structural properties of dendrimers such as size, shape, surface and interior chemistry, flexibility, and topology leading to the exact molecular weight with desired structural composition.

There are three main synthetic strategies in generating monodispersed macromolecules:3 the divergent strategy of Tomalia and co-workers, convergent synthesis of Fréchet and Hawker, and self-assembly strategy of Zimmerman and co-workers. In the divergent synthesis, dendrimers are built outward from the core to periphery. The first generation of dendrimer is synthesized by attaching branching units onto the reactive central core, and then the functional periphery of the molecule is activated for the second generation with more branching units. The required degree of generations in the dendrimer results from the controlled and repetitive reaction between functional groups on the surface and branched building block. Despite the synthetic advantages for the preparation of very large size of dendrimers in this way, side products generated from the incomplete growth steps can lead to the difficulty in isolation and characterization of desired pure dendrimer, even with very efficient reaction conditions.2

To overcome the weaknesses of divergent synthesis, the convergent strategy was developed by Fréchet and Hawker in 1989-1990. As opposed to divergent methodology, convergent synthesis starts from outside end groups, which end up being
the surface of the dendrimer, and then keep building up more monomers inwards until the required generations are reached. Finally, the prepared large branching building blocks (called dendrons) are attached to a reactive central core molecule to produce a desired dendrimer. Moreover, this convergent growth allows the efficient purification and isolation of a desired and well-defined dendrimers because the mass difference between any by-products and the pure product is quite large. However, convergent growth have a difficulty in producing high yields of large macromolecules because the steric hindrance in the focal points of the growing dendron prevents the complete reaction, and causes decreased yields of dendrimers.\textsuperscript{4}

\textbf{Figure 1.2.} Synthetic approaches.
Conjugated polymers have been investigated as fascinating materials which exhibit valuable properties and applications in electronics and optoelectronics such as optical sensing, energy transport, biosensor, and organic light-emitting diodes (OLEDs) over the past two decades. These properties of conjugated materials accommodate the examination of energy and charge transfer mechanisms. In organic light-emitting diodes (OLEDs), optoelectronic properties depend on the close intermolecular interactions of emissive chromophores that result in excimer formation and reduced light emission.

However, polymers that exhibit the aggregation of $\pi$-conjugated systems often result in low quantum efficiency for the luminescence property. One of the main reasons for this is that the long chains of linear polymers aggregate together, and lead to the poor close packing of a conjugated system. Thus, the problems in packing result in poor charge injection and transport. Unlike conjugated linear polymers, conjugated dendrimers that consist of self-similar shapes of branching geometry are readily amenable to structural modification to resolve the aforementioned problems in OLEDs. The well-defined structures of dendritic macromolecules can reduce strong intermolecular interactions and aggregation. Therefore, conjugated dendrimers exhibit various potential properties in terms of photo- and electroluminescence as well as the durability of electronic devices.

Conjugated dendrimers, which contain extended $\pi$-electron systems, allow for large absorption across a wide range of the visible spectrum and excitation at a
chromophore unit in the surface of the dendrimers, and then the energy is transferred to a core with a smaller HOMO-LUMO energy gap along the conjugated chains.\textsuperscript{5}

2.1 Approach

Our interest involves exploration into the design and syntheses of novel organic molecular architectures, which we term “spider-web” dendrimers (Figure 2.1). These “spider-web” dendrimers differ from traditional dendrimers by possessing rigid, flat, 2-dimensional architectures as well as an extended $\pi$-conjugated system. Such structures (1-3) are not only intriguing from a synthetic standpoint, but also for the incorporated properties. These “flat” dendrimers (1-3) redefine the definition of a conventional dendrimer, which is a 3-dimentional, branched, monodispersed macromolecule with a spherical shape.

The flat dendrimers will have increased conjugation because of the stretch of a conjugated system with a rigid and flat configuration. These spider web type dendrimers consist of a hexavalent aromatic core and rigid ethynyl units linked by ether chains. The ether chains prevent rotation about the single bonds, as well as, increases solubility. These hexaethynylbenzene and hexaethynyltriphenylene units in the center of proposed dendrimers will have intriguing properties. The flat dendrimers can easily be modified to be useful as liquid crystalline materials, nonlinear optical (NLO) materials, or potential as precursors of well defined molecular fragments representing novel two-dimensional carbon network. In addition to the extended $\pi$-conjugation, these hexaethynylbenzene and hexaethynyltriphenylene derivatives are effective for the preparation of divergent dendrimeric moieties.\textsuperscript{8}
Figure 2.1. “Spider-web type” flat dendrimers.
The proposed dendrimers (1-3) have a flat configuration because the ethynyl units are “locked” in place by the ether connections. One of the main emphases of the work on these flat dendrimers is developing effective materials for the energy transfer. These ethynyl dendrimers are expected to show directed energy and electron transfer due to the highly conjugated system where electrons are fully delocalized, and as a result, maybe useful in the preparation of photo-reactive materials such as electronic sensor or light harvesting materials.

Light-emitting dendrimers that consist of an emissive core, dendrons, and multifunctional surface end-groups, can control the interactions of the emissive and charge transporting chromophores by the control of structural design in the macromolecules.

Jeffrey Moore, who is faculty member at the University of Illinois, has studied the light harvesting properties of conjugated dendrimers. Moore⁹ has prepared a large number of phenylacetylene dendrimers, which show directed energy and electron transfer and are useful in the preparation of photoreactive materials. Jeffrey Moore’s dendrimers also have the alkyne connected conjugated system with benzene core (Figure 2.2). However, in Moore’s systems the efficiency of the intramolecular energy transfer decreases with increasing dendrimer size. This decrease in energy transfer is presumably due to twisting around the single bonds of the dendrons, resulting in loss of conjugation and reduced light harvesting throughout the structure.

On the other hand, flat dendrimers (1-3) cannot lose the conjugation because the ethynyl units are locked in place by the ether connections, producing a more highly
conjugated system. Therefore, this flat and rigid configuration of dendrimers 1-3 allows these dendrimers to be prospective light harvesting candidates.

Figure 2.2. Jeffrey Moore’s conjugated phenylacetylene dendrimer.

2.2 Applications

The proposed “spider web” type dendrimers can be modified to promote additional supramolecular behaviors which may act as discotic liquid crystals. Liquid crystals are fluids showing specific properties between those of a flow-like liquid and a well-ordered, crystal-like solid. Discotic liquid crystals have a flat rigid core, a disc-like mesogen, and are surrounded by flexible aliphatic side chains. They tend to stack on the top of one another typically due to π-π interactions. Various discotic liquid crystals are categorized by the type of ordering in structural phases that include positional order,
orientational order, and short-range or long-range order between molecules close to each other. There are two main types of discotic liquid crystals, nematic phase and columnar phase (Figure 2.3). The nematic phase is orientationally ordered in the same direction, but is not positional ordered, which means the center of the molecules, is randomly distributed. On the other hand, the columnar phase assembles themselves, one on top of one another, forming column-like structure, which orient in a two-dimensional lattice of the columnar packing.¹⁰

Figure 2.3. Discotic columnar stacks.

Based on their alignment and dynamics, columnar discotic liquid crystals have been used in fascinating electronic devices such as light-emitting diodes (LED), photovoltaic diodes (PVD), field effect transistors (FET), memory elements and sensors.¹¹

Columnar discotic liquid crystals allow energy migration because of the close overlap of the \( \pi \)-electron orbitals between the adjacent aromatic cores.¹² It can act like ‘molecular wires’ with the charge carriers because the well-ordered columnar stack allows the transport of electronic charges via hopping between aromatic rings along the
Moreover, the surrounding aliphatic side chains insulate each column from its neighbors.

Two of the most well known representatives of discotic liquid crystals forming the perfection of order within column are shown in Figure 2.4. These benzene and triphenylene derivatives have a flat rigid core and are surrounded by aliphatic side chains.

Figure 2.4. Known discotic liquid crystals.

Like the known discotic liquid crystalline materials, the proposed “spider-web” type flat dendrimers (1-3) also have a rigid, flat and 2-dimensional structure. The flat dendrimers with appropriate alkyl side chains (R groups) are predicted to associate to form columnar stacks due to the aromatic stacking interactions. Such materials self-organize to form liquid crystal phases and studies in this area are planned. In addition, the flat dendrimers (1-3) contain a larger flat rigid core center than known discotic liquid crystals, which have only benzene or triphenylene cores. Therefore, if liquid crystalline
properties are observed in these materials, they would have the largest core sizes known and would allow investigation into the effects of core size on the discotic properties.

![Dendritic rotaxanes](image)

Figure 2.5. Dendritic rotaxanes.

More long-term goals, of the proposed flat dendrimers, include investigation into the cation binding abilities of the crown ether linkages contained within the macromolecular structure and investigation into the use of these structures to build the first rotaxane dendrimers. The proposed flat dendrimers are highly electronegative due to the electron transfer in the conjugated system and electron-donating ether chains. The dendrimers 2 and 3 have internal cavities of different sizes and therefore, could capture a variety of cations. For example, any positive charged atoms or
molecules, such as sodium cations, potassium cations or ammonium compounds could be encapsulated by these cavities (Figure 2.5). Therefore, the flat dendrimers, described here, can be applied to many diverse areas such as electric sensors, light harvesting materials, drug deliveries and water purification.

2.3. Synthetic Strategy for Building Flat Dendrimers

The synthetic design of these macrocyclic dendrimers is very important. Cyclization must occur in a systematic stepwise fashion in order to avoid undesired cyclized side products. The undesired cyclization pathway B (Figure 2.6) can be avoided by alternating the functional groups on each arm of the hexa-substituted benzene. This allows for ring closure to happen in a stepwise fashion. The second undesired dual cyclization pathway, C, (Figure 2.6) is avoided by selection of a connective ether chain of the proper length. Therefore, desired cyclization pathway A will be achieved by alternating functional groups on the each benzene branching units of the hexa-substituted benzene core as well as selecting of right size of ether chain.

A divergent synthetic method, which starts from a central core and builds outward, was chosen for the synthesis of the proposed “spider-web” type dendrimers (1-3). These proposed dendrimers involve hexaethynyl benzene or hexaethynyl triphenylene moiety in the configuration.
2.4. Results and Discussion

2.4.1 Dendrimer 1

For the preparation of the proposed dendrimers, first, palladium catalyzed selective alkynylation of polyhaloarenes has been considered. The differentially substituted hexaethynylbenzene derivatives have been synthesized effectively by the Sonogashira coupling reaction of halobenzene with terminal acetylenes. The alkynylation would be selective toward iodo groups in the presence of bromo groups on a 1,3,5-tribromo-2,4,6-triiodo benzene core. This selectivity allows for the dual coupling reactions of 1,3,5-tribromo-2,4,6-triiodobenzene with terminal acetylene arms with alternating functional groups on a benzene core, and produces a differentially functionalized hexaethynyl benzene derivatives with $D_{3h}$ symmetry. According to a published report, 1,3,5-tribromo-2,4,6-triiodo benzene was prepared in 38% yield from
the reaction of 1,3,5-tribromobenzene with bis(pyridine)iodonium tetrafluoroborate, trifluoromethane sulfonic acid in dry dichloromethane. However, in spite of this easy introduction of branching units on this core, the coupling reaction condition prevented any type of selective alkynylation because of very poor solubility of the reactants. This resulted in several by-products, mono-, bis-, tris-, tetrakis-, or pentakis-, hexakis ethynyl benzenes, from the reaction of 1,3,5-tribromo-2,4,6-triiodobenzene with terminal acetylenes.18

Rubin and coworkers19 have reported a remarkably efficient synthetic methodology for the preparation of 1,3,5/2,4,6 differentially functionalized hexaethynylbenzene derivatives through the stepwise construction. This synthetic method begins with the Pd-catalyzed coupling of the 2,4,6-tribromobenzene-1,3,5-tricarboxaldehyde (prepared from mesitylene) with terminal acetylene to provide the 2,4,6-triethynylbenzene-1,3,5-tricarboxaldehyde. This is followed by the Corey-Fuchs dibromo-olefination20 and treatment with lithium diisopropylamide (LDA) to generate the respective hexaethynyl compound. Finally, another coupling reaction with a terminal acetylene produces the 1,3,5/2,4,6 differentially functionalized hexaethynylbenzene derivatives.

To make the desired cyclized dendrimer 1 in Scheme 2.1, we have considered Rubin’s synthetic route, and come up with three starting materials. There are two branching units, which are the protected benzylalcohol bromobenzene compound 4 and tribromobenzene-1,3,5-tricarboxaldehyde 6. After preparation of these compounds by multi-step syntheses, the branching unit 5 will be attached to the meta position of
Scheme 2.1. Preparation of dendrimer 1.

protected phenol ethynylbenzene compound 5. The core for dendrimer 1 is 2,4,6-benzene core using a Sonogashira coupling reaction, and followed by another coupling reaction using branching unit 4 on the respective ethynyl groups produced from the aldehyde groups. As a result of the coupling reactions, 1,3,5/2,4,6 differentially functionalized hexaethynylbenzene will be generated. Later, the deprotection of the alcohols and ring closure by substitution of alkyl chains will generate the desired cyclic dendrimer 1.
Scheme 2.2. Preparation of the core molecule for dendrimer 1.

The synthesis of a core molecule 6 for dendrimer 1 is shown in Scheme 2.2. First, mesitylene 7 was halogenated by electrophilic aromatic substitution with bromine in the presence of Lewis acid catalyst. Recrystallization of the crude product from chloroform gave pure 1,3,5-tribromo-2,4,6-trimethylbenzene 8 in 84% yield. Further bromination of 8, via free radical addition on the benzyl position under light irradiation, yielded 1,3,5-tribromo-2,4,6-tris(bromomethyl)benzene 9 (80%) without any additional purification. The hexa-bromo compound 9 was subjected to a $S_N2$ reaction with sodium acetylate in dimethylformamide (DMF) to produced 1,3,5-tris(acetoxymethyl)-2,4,6-tribromobenzene 10 in 92% yield. Finally, hydrolysis of 10 with potassium hydroxide (giving 1,3,5-tribromo-2,4,6-tris(hydroxymethyl)benzene 11 in 84% yield) followed by oxidation using pyridinium chlorochromate (PCC), which is highly effective in oxidizing primary alcohol to corresponding aldehyde, hence produced the core molecule, 2,4,6-tribromobenzene-1,3,5-tricarboxaldehyde 6 (70%).
With the core molecule synthesized, focus now turns to the two branching units. The preparation of the branching unit 4 from dimethyl-5-bromoisophthalate 12 is shown in Scheme 2.3. The starting material 12 was purchased from Aldrich and reduced with lithium aluminum hydride to produce 3-bromo-5-(hydroxymethyl)phenyl-methan-1-ol 13 in 80% yield.

Scheme 2.3. Preparation of the branching unit 4 for dendrimer 1.

The next step involves the protection of the benzyl alcohol groups. The first consideration was to use a triisopropylsilyl (TIPS) protecting group. The general procedure for the silylation of alcohols was accomplished by using triisopropylsilyl chloride (TIPSCI) with a Cs$_2$CO$_3$ catalyst in DMF solvent and stirring for 2 days. However, the general protection method had difficulties in prolonged reaction times as well as tedious and time consuming work-up process because of the presence of DMF solvent. As a result of these problems, the yield of alcohol protected triisopropylsilyl compound was very low (30%). Recently, the use of microwave irradiation as an effective energy-transferring medium in organic reactions has attracted wide spread interest due to its short reaction times, operational simplicity, and avoidance of toxic
solvents such as DMF.\textsuperscript{22} The \textit{tert}-butyldimethylsilyl (TBDMS) group has also been used for the effective hydroxyl protection because of its easy introduction and removal under mild reaction conditions. \textit{tert}-Butylmethylsilyl chloride (TBDMSCl) is also relatively less volatile than triisopropylsilyl chloride (TIPSCI) in microwave irradiation conditions so that it results in the completion of protection with excellent yields. As a result of these advantages for optimization of protection reaction, the OH groups on benzyl position were protected using \textit{tert}-butylmethylsilyl chloride (TBDMSCl) and imidazole as a base under microwave irradiation to produce alcohol protected branching unit 4 in 93% yield.

As shown in Scheme 2.4, synthesis of branching unit 5 began with the alcohol protection of 3,5-dihydroxybenzaldehyde 14 with TBDMSCl and imidazole base under microwave irradiation to give the corresponding alcohol protected benzaldehyde 15 in very high yield (100%). Compound 15, containing aldehyde groups, underwent Corey-Fuchs olefination with carbon tetrabromide and triphenylphosphine in dry dichloromethane to produce a 70% yield of dibromo-olefin 16. However, in the presence of zinc powder catalyst, the yield increased to 100%. In the final step, compound 16 was easily converted into the respective ethynyl compound 5 in 88-100% yield by treatment with \textit{n}-BuLi at -78 °C.

Sonogashira coupling reactions were used to attach the two branching units 4 and 5 were to the prepared core compound 6. As shown in Scheme 2.7, the first step is attaching the branching unit 5 onto the central core molecule 6. This step has been a struggle. The reaction has been tried many times using a variety of Pd catalysts, such as (PPh\textsubscript{3})\textsubscript{2}PdCl\textsubscript{2}, Pd\textsubscript{2}(dba)\textsubscript{3}, and Pd(PPh\textsubscript{3})\textsubscript{4}, and different reaction conditions. However, the desired product 17 was produced in low yields with the reaction mixture containing a
small amount of unreacted starting materials and a major by-product, which is the homocoupling dimer of the starting ethynyl compound.

Scheme 2.4. Preparation of the branching unit 5 for dendrimer 1.

The palladium-catalyzed coupling reaction between aryl halides and terminal alkynes in the presence of a copper (I) co-catalyst has received considerable attention for the preparation of arylalkynes and conjugated compounds.

Sonogashira coupling reaction is a very sensitive and tricky reaction. This coupling reaction never shows constant behavior even in the same conditions. The reactivity in the Sonogashira process frequently depends on the purity of the reactants. In most cases, high yields of the desired product result only from reaction with relatively more reactive iodoarenes over chloro- and bromoarenes. The use of higher temperatures, long reaction time and the presence of copper co-catalyst are associated with undesired homocoupling reactions of the terminal acetylenes. For alternatives to the Cu(I)I co-catalyst, copper free methodologies have been developed to overcome the problem of the competitive homocoupling to give the diyne.23
As a starting point for the development of the coupling methodology, we have varied the palladium catalyst loading, with or without the use of Cul co-catalyst, temperature, reaction times, as well as the basic solvents which involve triethylamine, piperidine, and 1,4-dioxane.

Negishi coupling reaction (Scheme 2.5) is one of the copper free methods for the synthesis of biaryls and styrene derivatives. The reaction represents palladium-catalyzed cross-coupling of aryl and vinyl halides with organozinc reagents. In particular, the Negishi reaction efficiently cross-couples relatively unreactive aryl and vinyl chlorides with organozinc reagents.

![Scheme 2.5. Negishi coupling reaction.](image)

A trial reaction (chlorobenzene with trimethylsilane) was carried out using Negishi coupling conditions as shown in Scheme 2.5. 2.5 M n-BuLi in n-hexane was added dropwise to the acetylene solution at -78 °C. A solution of anhydrous zinc chloride in THF was then added dropwise to produce (phenylethynyl)zinc chloride. To a two-necked round-bottomed flask, chlorobenzene and Pd(PPh₃)₄ were dissolved in THF, and a solution of prepared (phenylethynyl)zinc chloride was added. The resulting mixture was then slowly warmed to room temperature, followed by stirring and refluxing for 3 days. However, only starting compounds were recovered without any desired product.
While struggling with the coupling reaction, we found the copper (I) iodide that was being used was bad. Copper (I) iodide is very moisture and light sensitive, which can result in easy oxidation into copper (II) oxide. The color of fresh copper (I) iodide should be white, but the copper iodide that was being used was dark gray color, which is indicative of copper (II) oxide. When copper (II) iodide serves as an oxidizing agent, a radical reaction occurs with the formation of an acetylenic radical and produced the major homocoupling diyne by-product as outlined in Scheme 2.6.28,29

\[
\begin{align*}
R \equiv H & \quad \xrightarrow{\text{base}} \quad R \equiv \Theta & + H^+ \\
R \equiv \Theta & \quad + \quad \text{Cu}^{2+} \quad \rightarrow \quad R \equiv \cdot & + \quad \text{Cu}^+ \\
2 \quad R \equiv \cdot & \quad \rightarrow \quad R \equiv \equiv \equiv \equiv \equiv R
\end{align*}
\]

Scheme 2.6. Oxidative homocoupling reaction.

Therefore, the role of copper(I) iodide is very important to facilitate the coupling reaction of acetylenes. With this in consideration, the Sonogashira coupling was carried out with fresh white copper (I) iodide that was added to a mixture of fresh white copper (I) iodide that was added to a mixture of bis(triphenylphosphine)palladium dichloride and 2,4,6-tribromobenzene-1,3,5-tricarboxaldehyde 6 in THF and triethylamine solvents in a nitrogen. The solution of acetylene 5 in THF was slowly added to the reaction mixture, stirred at 40 °C for 2 hours, treated with saturated NH₄Cl, and extracted with dichloromethane.

After purification by flash column chromatography on silica gel, the desired product 17 was obtained in 60% purified yield. Compound 17, containing aldehyde groups on benzene core, was subjected to Corey-Fuchs dibromo-olefination with CBr₄,
PPh$_3$, and Zn dust in dichloromethane for 5 days. The reaction progress was monitored by TLC. The reaction mixture was filtrated through a plug of silica gel, eluting with hexanes/ethyl acetate (20:1). However, the resulting isolated compound was not the desired product 18. Once the dibromo-olefination reaction conditions are worked out, the next respective hexaethynyl compound 19 will be obtained by treatment of 18 with $n$-BuLi.

Scheme 2.7. Attachment of branching unit to the core.

The next step (Scheme 2.8) involves attaching the second branching unit 4 via Sonogashira reaction and producing the 1,3,5/2,4,6 differently functionalized
hexaethynylbenzene 20.

The last approach for the synthesis of dendrimer 1 is alcohol deprotection. The OH protected groups on phenyl position will be deprotected with hydrofluoride and then replaced by ether chains via SN2 reaction, using an excess amount of 1,3-dibromopropane in a weak basic condition (potassium carbonate) to give 21. The reaction of OH groups on the benzylic position with the stronger base, sodium hydride and under dilute condition will finally produce cyclized dendrimer 1.

**Scheme 2.8.** Last approach for the synthesis of dendrimer 1.
2.4.2 Dendrimer 2

The retrosynthesis of proposed dendrimer 2 is shown in Scheme 2.9. The core molecule is this 2,3,6,7,10,11-hexaethynyltriphenylene 23. The branching unit 22a has alternated functional groups on the benzene ring to make desired cyclization to give dendrimer 2. With the preparation of these two stating materials, the desired “spider-web” type dendrimer 2 can be developed by divergent methodology.

Scheme 2.9. Preparation of dendrimer 2.
Scheme 2.10. Preparation of the core molecule for dendrimer 2.

Scheme 2.10 shows the preparation of the core molecule 23 for dendrimer 2. First, triphenylene 24 underwent electrophilic aromatic substitution with bromine and a Lewis acid, iron catalyst in nitrobenzene followed by recrystallization from ortho-dichlorobenzene to give white needles of 2,3,6,7,10,11-hexabromotriphenylene 25 in 80% isolated yield. This hexabromotriphenylene 25 was alkynylized by Sonogashira coupling reaction with ethynyltrimethylsilane in the presence of PdCl₂(PPh₃)₂ and CuI catalysts in triethylamine for 3 days, and produced 65% of 2,3,6,7,10,11-hexakis(2-(trimethylsilyl)ethynyl)triphenylene 26. Hydrolysis of compound 26 was accomplished with potassium carbonate in methanol/dichloromethane to produce 91% of 2,3,6,7,10,11-hexaethynyltriphenylene 23 as a core molecule for dendrimer 2.
The preparation of the branching unit for dendrimer 2 is shown in Scheme 2.11. The preparation began with the partial reduction of one of the two nitro groups of 3,5-dinitrobenzoic acid 27 with hydrazine and Raney nickel, as a catalyst, in water. After reflux for 7-8 hours, the reaction mixture was filtered and made acidic (pH = 3.5) with aqueous HCl. The product, 3-amino-5-nitrobenzoic acid 28, was isolated as a yellow solid in 40% yield.

\[
\begin{align*}
\text{27} & \quad \text{O}_2\text{N} \quad \text{O} \quad \text{H}_2\text{N} \quad \text{O}_2\text{N} \quad \text{O} \\
\text{NH}_2\text{NH}_2, \text{Ni} & \quad \text{H}_2\text{O} \quad 40\% \\
\text{28} & \quad \text{NaNO}_2, \text{KI} \quad \text{HCl, H}_2\text{O, 0}\text{°C} \quad 61\% \\
\text{29} & \quad \text{NaNO}_2, \text{H}_2\text{SO}_4 \quad \text{CuNO}_2, \text{Cu}_2\text{O} \quad 92\%
\end{align*}
\]

**Scheme 2.11.** Preparation of the branching units 22a and 22b for dendrimer 2.

Compound 28, containing an amino group, formed the diazonium salt, which can be easily replaced by a number of groups including halide ions, using nitrous acid (formed in situ from sodium nitrite and acidic conditions). The diazonium salt underwent a Sandmeyer reaction with potassium iodide to give 3-iodo-5-nitrobenzoic acid 29 in a
61% yield. Next, the carboxylic acid group of compound 29 was reduced with BH$_3$-THF under nitrogen atmosphere to form a 78% yield of corresponding benzylalcohol, (3-iodo-5-nitrophenyl)methanol 30. The reaction of carboxylic acids with BH$_3$-THF shows remarkably rapid and highly selective reduction to make corresponding alcohol. The nitro group of compound 30 was reduced by tin chloride in an acidic environment to produce an 80% yield of the amino compound, (3-amino-5-iodophenyl)methanol 31. The next step is introducing a hydroxyl group from a solution of the corresponding diazonium salt. The amino compound 31 formed a diazonium salt with sodium nitrite in sulfuric acid. This was followed by a reduction of the diazonium ion by a cuprous ion, involving cupric nitrite and cuprous oxide catalyst. In this reaction, an aryl radical is formed as an intermediate. The aryl radical was hydrolyzed in weakly alkaline aqueous solution by the addition of 1 N NaOH. The crude product was purified by flash column chromatography to give 92% of 3-(hydroxymethyl)-5-iodophenol 32. Last step for the preparation of branching unit 22a for dendrimer 2 was the protection of the hydroxyl groups with tert-butyldimethylsilyl chloride (TBDMSI) and imidazole base catalyst under microwave irradiation to make the alcohol protected iodobenzene compound 22a in 90% yield.

Scheme 2.12 shows the overall final scheme for the synthesis of dendrimer 2. The prepared core molecule 23 and branching unit 22a or 22b, from the previous Schemes 2.10 and 2.11, will be coupled together by Sonogashira coupling reaction in the presence of palladium catalyst and copper (I) iodide co-catalyst. The last approach for the synthesis of dendrimer 2 involves deprotection of the alcohol with hydrofluoride in acetonitrile. Ether chains will replace the subsequent phenol groups, using 1,3-
dibromopropane, via $S_N$2 reaction under dilute condition and a weak base (potassium carbonate).

Scheme 2.12. Last approach for the synthesis of dendrimer 2.
The final reaction involves the reaction of the hydroxyl groups at the benzyl position with a stronger base, sodium hydride, followed by an $S_N\text{2}$ reaction with 1-(2-bromoethoxy)-2-bromoethane. As a result of the substitution, the branching units attached on the central core will be closed by proper length of ether chains and produce the desired “spider-web” type flat dendrimer 2.

2.5 Conclusions

The research presented here is mainly focused on synthesis, characterization, and analysis of conjugated flat dendrimers. By the careful design of the specific starting materials described in this chapter, the construction of the desired architectures of “spider-web” type flat dendrimers can be achieved. The “flat,” 2-dimensional dendrimers described here are the first of their kind and are the sole examples of a new class of macromolecular architecture. Further study of these novel dendrimers will determine electronic and discotic liquid crystalline properties as well. The proposed conjugated flat dendrimers are expected to have several applications in many diverse fields such as electronic sensors, light harvesting materials, and drug deliveries, etc. Furthermore, these types of dendrimers will be extended with the stretch of conjugated system by constructing larger generations.

2.6 Experimental

**General Methods.** Unless otherwise stated, all starting materials were purchased from Aldrich Chemical Co. and were used without further purification. All atmosphere sensitive reactions were carried out under nitrogen, over an anhydrous
calcium sulfate gas-drying unit. Solvents used, were of reagent grade and purified by standard methods: diethyl ether was distilled over sodium/benzophenone, triethylamine was distilled over calcium hydride, tetrahydrofuran was distilled over potassium/benzophenone, and dimethylformamide was distilled over anhydrous magnesium sulfate. All NMR solvents (CDCl₃, with or without tetramethylsilane, TMS) were stored over 4 Å molecular sieves prior to use. Analytical TLC was performed on aluminium backed, pre-coated silica gel plates and visualization was accomplished with UV light. Flash column chromatography was carried out with silica gel (60Å mesh) from 40-63µm.

NMR spectra were obtained at room temperature with a Varian VXR-500 spectrometer, operating at frequencies of ¹H 499.82 MHz and ¹³C {¹H} 125.67 MHz, respectively, or a Varian Gemini-200 spectrometer, operating at frequencies of ¹H 200.0 MHz and ¹³C {¹H} 50.3 MHz, employing a deuterium sample of internal lock unless noted otherwise. The ¹H chemical shifts are reported relative to CHCl₃ (7.24 ppm) and ¹³C {¹H} chemical shifts are reported relative to CDCl₃ (77.0 ppm). Reported melting points were obtained with a Mel-Temp® capillary apparatus and are uncorrected.

![3-Bromo-5-(TBDMS protected hydroxymethyl)phenyl-methan-1-ol (4).](image)

3-Bromo-5-(TBDMS protected hydroxymethyl)phenyl-methan-1-ol (4).

3-Bromo-5-(hydroxymethyl)phenyl-methan-1-ol 13 (900 mg, 4.14 mmol), tert-butyl(dimethyl)silyl chloride (2.50 g, 16.6 mmol), imidazole (1.69 g, 24.8 mmol) and a boiling chip were added and mixed in a dry vial and then irradiated at 30 W for 30
seconds in a conventional microwave oven. TLC indicated completion of the reaction. The resulting mixture was extracted with ether and washed with water. The organic solvent was evaporated under reduced pressure. The resulting mixture was purified by column chromatography eluting with hexanes/ethyl acetate (4:1) to give the product as transparent oil (2.00 g, 92%). $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ 7.38 (s, 2H), 7.24 (s, 1H), 4.71 (s, 4H), 0.96 (s, 18H), 0.12 (s, 12H).

5-ethynylbenzene-1,3-TBDMS protected diol (5). A solution of starting material 16 (300 mg, 0.574 mmol) in 3 mL hexanes was cooled at -78 °C. 2.5 M $n$-butyllithium in hexanes (1.15 mL, 2.87 mmol) was slowly added dropwise under nitrogen atmosphere. The reaction mixture was stirred for 2 hours at -78 °C and then allowed to come to room temperature. Saturated aqueous NH$_4$Cl solution was added and the mixture extracted with diethyl ether. The combined organic fractions were dried under MgSO$_4$, filtered and evaporated in vacuo. The mixture was purified by column chromatography on silica gel (hexanes/ethyl acetate= 9:1) yielding 5 as transparent oil (208 mg, 100%). $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ 6.58 (d, $J$= 2.2 Hz, 2H), 6.36 (t, $J$= 2.2 Hz, 1H), 2.99 (s, 1H), 0.96 (s, 18H), 0.18 (s, 12H).
2,4,6-tribromobenzene-1,3,5-tricarboxaldehyde (6). To PCC (28.0 g, 0.3 mol) in dichloromethane (1.8 L) was added celite (10.0 g) and 4 Å molecular sieves (10.0 g), followed by 1,3,5-tribromo-2,4,6-tris(hydroxymethyl)benzene 11 (7.0 g, 17.5 mmol). The mixture was stirred vigorously at room temperature for 2 days, filtered through a pad of silica gel eluting with dichloromethane and the solvent evaporated to yield pure 2,4,6-tribromobenzene-1,3,5-tricarboxaldehyde as fluffy white needles (4.91 g, 70 %). $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ 10.13 (s, 3H).

1,3,5-tribromo-2,4,6-trimethylbenzene (8). To a 1 L three-necked round-bottomed flask containing iron powder (2.51 g, 45.0 mmol) and bromine (122 g, 76.0 mmol) and fitted with appropriate vents, to accommodate copious quantities of HBr gas produced by the reaction, was added 1,3,5-trimethylbenzene 7 (16.7 g, 139 mmol) slowly for 3.5 hours at room temperature. The reaction mixture was stirred for 3 days to generate a reddish-brown sludge. After addition of water, the crude product was filtered and recrystallized from chloroform to give colorless fine needles (41.7 g, 84%).
1,3,5-tribromo-2,4,6-tris(bromomethyl)benzene (9). To 1,3,5-tribromo-2,4,6-trimethylbenzene 8 (25.0 g, 70.1 mmol) in dried dichloromethane (600 mL) in a 1-liter round-bottomed flask equipped with a reflux condenser was added bromine (43.3 g, 0.271 mol) over 30 minutes while irradiating with a sun lamp. The mixture was heated to reflux for 1 day and treated with hexanes to give the product (33.0 g, 80%). $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ 4.96 (s, 6H).

1,3,5-Tris(acetoxymethyl)-2,4,6-tribromobenzene (10). To dry dimethylformamide (150 mL) was added 1,3,5-tribromo-2,4,6-tris(bromomethyl)benzene 9 (30.0 g, 50.0 mmol) and sodium acetate (30.0 g, 0.300 mol). The mixture was heated to 70 °C, stirred overnight, cooled, filtered to remove excess potassium bromide and poured into dichloromethane (1.1 L). The organic layer was extracted with water (5 times with 700 mL), then twice with brine. The solvent was evaporated to give the product (24.7 g, 92%): mp 149-151 °C. $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ 5.60 (s, 6H), 2.24 (s, 9H).
1,3,5-Tribromo-2,4,6-tris(hydroxymethyl)benzene (11). To 1,3,5-
Tris(acetoxymethyl)-2,4,6-tribromobenzene 10 (23.0 g, 44.2 mmol) was added distilled
water (500 mL) and KOH (30 g, 0.54 mol). The mixture was heated to reflux for 24
hours and cooled. The colorless solid was filtered off washed with water, acetone and
ether. The crude solid was recrystallized from 1-propanol yielding colorless fine needles
(15.1 g, 84%): mp 269 °C.

3-Bromo-5-(hydroxymethyl)phenyl-methan-1-ol (13). To a suspension of
lithium aluminum hydride (1.10 g, 28.9 mmol) in dry THF (80 mL) was added dropwise a
solution of dimethyl-5-bromoisophthalate 12 (6.00 g, 22.0 mmol) as a solution in dry
THF (80 mL) over 10 minutes. The mixture was then heated to reflux for 1 hour and
allowed to cool. To the mixture, was added dropwise a saturated solution of sodium
sulfate over 10 minutes. The ether layer was removed and the precipitate was washed
with additional ether. The combined ethereal solution was washed with saturated brine,
dried over sodium sulfate and concentrated on a rotary evaporator to give 13 as
colorless fine crystals (3.90 g, 83%). \(^1H\) NMR (200 MHz, acetone-d\(_6\)) \(\delta\) 4.39 (d, \(J=5.4,\ 5H\)), 4.62 (d, \(J=5.4,\ 13H\)), 7.31 (s, 3H), 7.41 (s, 6H).
3,5-TBDMS protected dihydroxybenzaldehyde (15). 3,5-dihydroxybenzaldehyde 14 (100 mg, 0.460 mmol), tert-butyldimethylsilyl chloride (0.395 mL, 1.84 mmol), imidazole (188 mg, 2.76 mmol) and a boiling chip was added and mixed in a dry vial and then irradiated at 30 W for 30 seconds in the microwave oven. TLC indicated completion of the reaction. The resulting mixture was extracted with ether and water. The solvent was evaporated under reduced pressure. The resulting mixture was purified by column chromatography (hexanes/ethyl acetate= 4:1) to give the product (15) as a slightly yellow liquid (167 mg, 99%). $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ 9.86 (s, 1H), 6.92 (d, $J$ = 2.2 Hz, 2H), 6.58 (t, $J$ = 2.2 Hz, 1H), 0.98 (s, 18H), 0.19 (s, 12H).

5-(2,2-dibromovinyl)benzene-1,3-TBDMS protected dihydroxydiol (16). The solution of the dibromo olefination reagent was prepared by stirring PPh$_3$ (1.43 g, 5.46 mmol), CBr$_4$ (1.81 g, 5.46 mmol), and Zn (0.356 g, 5.46 mmol) in dry dichloromethane (60 mL) overnight. The aldehyde 15 (0.500 g, 1.36 mmol), dissolved in dry dichloromethane (14 mL), was dropped slowly into the reaction mixture. After 2 days, the solution was filtered through a plug of silica gel, eluting with dichloromethane. Evaporation of the solvent led to pale yellow liquid of pure product (0.69 g, 97%). $^1$H
NMR (200 MHz, CDCl₃) δ 7.38 (s, 1H), 6.64 (d, J= 2.2 Hz, 2H), 6.32 (t, J= 2.2 Hz, 1H), 0.96 (s, 18H), 0.19 (s, 12H).

2,4,6-tris(2-(3,5-TBDMS protected dihydroxyphenyl)ethynyl)benzene-1,3,5-tricarboxaldehyde (17).³² To a solution of 2,4,6-tribromobenzene-1,3,5-tricarboxaldehyde 6 (300 mg, 0.752 mmol), Pd(PPh₃)₂Cl₂ (22.7 mg, 0.032 mmol), CuI (9.6 mg, 0.050 mmol) in THF and Et₃N was added ethynyl compound (982 mg, 2.71 mmol) in 2 mL THF. The mixture was stirred at 65 °C for 2 hours, and then treated with saturated NH₄Cl, poured into CH₂Cl₂, and extracted. The organic layer was washed with 1 N HCl, H₂O, and saturated NaCl. The solvent was evaporated under reduced pressure and purified by column chromatography on silica gel eluting with hexanes/ethyl acetate (15:1) to give the product (896 mg, 96%). ¹H NMR (500 MHz, CDCl₃) δ 10.83 (s, 3H), 6.76 (d, J= 2.0 Hz, 6H), 6.412(t, J= 2.0 Hz, 3H), 0.97 (s, 54H), 0.21 (s, 36H); ¹³C NMR (125 MHz, CDCl₃) δ 189.69, 156.97, 136.61, 129.78, 122.82, 117.52, 119.42, 106.93, 82.68, 30.03, 18.46, -5.87.
3-(TIPS-protected hydroxymethyl)-5-iodo-TIPS-protected phenol (22b). 3- (hydroxymethyl)-5-iodophenol 32 (49.2 mg, 0.197 mmol) was dissolved in 3 mL of dried DMF and then Cs$_2$CO$_3$ (385 mg, 1.18 mmol) were added at room temperature. The reactant was stirred for 1 day. After reaction, water was added and the crude product was extracted with ethyl acetate. The product was obtained by distillation (127 mg, 31 %). $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ 7.18 (s, 1H), 7.08 (s, 1H), 6.87 (s, 1H), 4.69 (s, 2H), 1.07 (br m, 42H).

2,3,6,7,10,11-hexaethynyltriphenylene (23). To a solution of 2,3,6,7,10,11-hexakis(2-(trimethylsilyl)ethynyl)triphenylene 26 (100 mg, 0.124 mmol) in methanol and dichloromethane (1:1) 5 mL was added potassium carbonate (Ca. 5.1 mg). The mixture was degassed and stirred under nitrogen atmosphere at room temperature for 12 hours. The solvent was removed under reduced pressure and the resulting residue purified by
flash column chromatography with ethyl acetate/hexanes (2:1) to give the product (42 mg, 91%). $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ 8.55 (s, 6H), 3.49 (s, 6 H).

2,3,6,7,10,11-Hexabromotriphenylene (25). To a solution of triphenylene 24 (2.00 g, 8.76 mmol) in nitrobenzene (80 mL) with Fe powder (0.180 g, 3.24 mmol) was added Br$_2$ (4.00 mL, 78.8 mmol) dropwise over 5 minutes. The solution was allowed to stand for 16 hours (solid separates, orange color), then heated under reflux at 205 °C for 2 hours (the dark brown solid dissolves, HBr is evolved and a new solid separates, orange color). The mixture was cooled to room temperature, mixed with 200 mL diethyl ether, and filtered. The crude product was recrystallized from 800 mL o-dichlorobenzene to yield 4.94 g (80%) of white needles.
2,3,6,7,10,11-Hexakis(2-(trimethylsilyl)ethynyl)triphenylene (26). A round-bottomed flask was charged with hexabromotriphenylene 25 (2.00 g, 2.85 mmol), PdCl$_2$(PPh$_3$)$_2$ (130 mg, 0.185 mmol), Cul (130 mg, 0.684 mmol), PPh$_3$ (262 mg, 0.998 mmol) and Et$_3$N (30 mL). After bubbling with N$_2$ for 1 hour, ethynyltrimethylsilane (0.70 mL, 4.8 mmol) was added by syringe under an N$_2$ atmosphere. The reaction mixture was stirred at 80 °C for 3 days. The solvent was removed under reduced pressure and the resulting residue was purified by flash column chromatography with hexanes to give the product (1.5 g, 65%). $^1$H NMR (200 MHz, CDCl$_3$) δ 8.57 (s, 6H), 0.36 (s, 54 H).

3-amino-5-nitrobenzoic acid (28). Raney Ni (0.4 g) was added to 3,5-dinitrobenzoic acid 27 (53.0 g, 0.250 mol) in 300 mL H$_2$O and hydrazine hydrate (43.8 mL, 0.900 mol). The mixture kept overnight, refluxed 7-8 hours until gas evolution ceased, cooled, filtered, and the filtrate made pH 3.5 with HCl. The product was isolated.
with yellow solids (24.3 g, 53%) $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ 8.22 (t, 1H), 7.61 (d, 2H), 4.18 (s, 2H).

3-iodo-5-nitrobenzoic acid (29). A heterogeneous mixture of 3-amino-5-nitrobenzoic acid 28 (15.2 g, 83.9 mmol) in 45 mL of concentrated HCl was stirred at 0 °C. The solution of NaNO$_2$ (8.70 g, 126 mmol) in 70 mL of ice water was added to the reaction solution. The resultant mixture solution was stirred at 0 °C for 1 hour, the added slowly with stirring to a solution of KI (48.8 g, 294 mmol) in 100 mL of water at 0 °C. The reaction mixture was slowly warmed to room temperature over 2 hours. The aqueous solution mixture was extracted with ethyl acetate, and the organic layer was washed with water, aqueous saturated sodium bicarbonate, and brine. The organic phase was dried over MgSO$_4$, filtered, and concentrated. The residue was purified by flash chromatography on silica gel with ethyl acetate/hexanes (7:3) to give the product (21 g, 84%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.58 (s, 1H), 8.66 (s, 1H), 8.73 (s, 1H). $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$ 165.80, 149.83, 145.06, 136.84, 135.20, 124.56, 94.26.

3-iodo-5-nitrobenzylalcohol (30). 3-iodo-5-nitrobenzoic acid 29 (500 mg, 1.70 mmol) in 2 mL of anhydrous THF was stirred and added 1 M BH$_3$-THF (8.5 mL, 8.5
mmol) at 0 °C for. The mixture solution was stirred and refluxed for 1 day. Excess borane was removed by addition of MeOH, and the solvents were evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (hexanes/ethyl acetate; 1:1) to give the yellow solid of product (370 mg, 78%).\textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{3}) δ 8.45 (s, 1H), 8.18 (s, 1H), 8.03 (s, 1H), 4.77 (s, 2H), 2.02 (br s, 1H).\textsuperscript{13}C NMR (50 MHz, CDCl\textsubscript{3}) δ 144.39, 141.20, 131.21, 120.72, 94.19, 63.17.

\textbf{3-amino-5-iodobenzylalcohol (31).} The solution of 3-iodo-5-nitrobenzyl alcohol 30 (1.44 g, 5.17 mmol), SnCl\textsubscript{2}•2H\textsubscript{2}O (7.00 g, 31.0 mmol) in HCl (10 mL) and acetic acid (15 mL) was gently warmed to 60 °C for one day. The reactant was made basic (pH = 10) with 40 % KOH solution and extracted with ethyl acetate. The mixture was purified by column chromatography (hexanes/ethyl acetate; 1:2) to give product (1.28 g, 62%).\textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{3}) δ 7.05 (d, J = 2.0 Hz, 1H), 6.94 (s, 1H), 6.61 (s, 1H), 4.52 (s, 2H), 3.67 (br s, 2H), 1.60 (br s, 1H).

\textbf{3-(Hydroxymethyl)-5-iodophenol (32).}\textsuperscript{33} 3-Amino-5-iodobenzyl alcohol 31 (100 mg, 0.402 mmol) was dissolved in 2 mL of hot 35 % sulfuric acid and then allowed to cool to below 15 °C. Ice (1.00 g) was added and the amine bisulfate precipitated. A
solution of sodium nitrite (36.0 mg, 0.523 mmol) in 1 mL of ice water was added dropwise under the surface of the ice-cooled solution with stirring at such a rate as to maintain the temperature at 0 °C. After the solution had been stirred for an additional 10 minutes, a few crystals of urea were added to decompose any excess NaNO₂. To the cold solution of diazonium bisulfate was added a solution of cupric nitrate trihydrate in 3 mL of H₂O (1.50 g, 6.31 mmol) at room temperature with vigorous stirring (the liquid rapidly changed to green color). Cuprous oxide (57.5 mg, 0.402 mmol) was added to the solution. The reactant solution was stirred at room temperature for 1 day. The mixture was filtered free of cuprous oxide. The filtrate was made basic by the addition of 1 N NaOH and the resulting solution was extracted with ethyl ether. The crude product was purified by column chromatography on silica gel (hexanes/ethyl acetate; 1:1) to give the product (49.2 mg, 49%) ¹H NMR (200 MHz, CDCl₃) δ 7.23 (s, 1H), 7.10 (s, 1H), 6.78 (s, 1H), 4.56 (s, 2H).

2,4,6-tris(2-(trimethylsilyl)ethynyl)benzene-1,3,5-tricarboxaldehyde (61). To a solution of 2,4,6-tribromobenzene-1,3,5-tricarboxaldehyde 6 (150 mg, 0.376 mmol), Pd(PPh₃)₂Cl₂ (32.0 mg, 0.00400 mmol), CuI (2.60 mg, 0.0140 mmol) in THF and Et₃N was added trimethylsilylacetylene (0.213 mL, 1.50 mmol). The mixture was stirred at 40 °C for 2 hours, treated with aqueous NH₄Cl, poured into CH₂Cl₂, and extracted. The
organic layer was washed with 1 N HCl, H₂O, and saturated NaCl. Drying and evaporation of solvent led to a gray solid, purified by column chromatography on silica gel eluting with hexanes/CH₂Cl₂ (1:1) to give white needles (71 mg, 42%). ¹H NMR (500 MHz, CDCl₃) δ 10.61 (s, 3H), 0.26 (s, 27 H); ¹³C NMR (125 MHz, CDCl₃) δ 190.0, 138.2, 128.5, 115.2, 96.8, 0.0.
CHAPTER 3
LUMINESCENT MATERIALS

3.1. Introduction to Luminescence

Chemical reactions, electrical energy, subatomic motions, and stress on a crystal can cause luminescence. Photoluminescence occurs when a molecule absorbs light resulting in an excitation of an electron from HOMO (highest energy occupied molecular orbital) to a higher energy level followed by subsequent emission of light leading to the relaxation, of the excited electron, back to the ground electronic state. There are two kinds of luminescence bands: fluorescence and phosphorescence. The Jablonski diagram (Figure 3.1) describes the relaxation mechanism of light emission for excited state molecules in luminophores. According to the selection rules of quantum mechanics, electronic transitions are allowed in the same spin multiplicity between ground and excited states. A fluorescent process is associated with the emission of light with the same spin multiplicity between the ground and excited states (S\(_1\)→ S\(_0\) in Figure 3.1). This spin-allowed transition occurs favorably and shows relatively short lifetimes of the excited states, typically <10\(^{-6}\) s. Unlike fluorescence, phosphorescence is a process in which the energy absorbed in a chemical substrate is released slowly in the form of light, and shows a longer lifetime of the excited state than fluorescence (typically range from 10\(^{-6}\) s to several seconds) because of the “forbidden” energy state transitions (triplet→singlet) in quantum mechanics. This intersystem crossing relaxation from S\(_1\) to T\(_2\) has an important role in luminescent properties of transition metal complexes containing heavy metal atoms as well as organic luminophores having iodine and bromine.
The common luminescence bands in most luminescent organic compounds are caused by $\pi^*-\pi$ and $\pi^*-n$ transitions and follow the spin selection rules, so that they exhibit strong fluorescence. On the other hand, the most luminescent inorganic compounds, containing metal ions and organic ligands, show the phosphorescence because the d-d transitions of heavy metal ions are forbidden transitions. Therefore, charge-transfer transitions such as LMCT (ligand-to-metal charge transfer) and MLCT (metal-to-ligand charge transfer) are relatively allowed.\textsuperscript{35}

These days, efficient luminescence materials of organic and inorganic origin have been developed to produce excellent quantum efficiencies, brightness, chromaticity, and long lifetimes.\textsuperscript{36}

### 3.1.1 Luminescent Transition Metal Complexes

Luminescent closed-shell transition-metal complexes have attracted considerable
attention in the diverse areas including light-emitting devices (LEDs), nonlinear optics, optical sensing of environmental pollutants, solar energy conversion, photocatalysis, luminescent probes for biological systems, optical telecommunication, photoinduced magnetic switching, optical writing, and semiconductive materials.\textsuperscript{37} Most luminescent closed-shell transition-metal complexes have several unique properties which involve weak metallophilic bonding in the ground state, as well as, covalent metal-metal bonding in low-lying excited states. These properties result in the formation of luminescent excimers and exciplexes with large Stokes shifts and phosphorescence.\textsuperscript{37} Most polynuclear conjugated organic luminophores exhibit fluorescent emissions, which are spin-allowed energy transitions with same spin multiplicity resulting in short lifetimes of the excited state at room temperature. In the case of spin-forbidden energy state transitions, these involve $S_1 \rightarrow T_2$ intersystem crossing and $T_1 \rightarrow S_0$ relaxation (Figure 3.1) and result in long lifetimes and low quantum efficiencies.\textsuperscript{38} This drawback for the low luminescence efficiency can by overcome by using phosphorescent heavy metal-organic luminophores. The transition metals with organic chromophores induce phosphorescence due to spin-orbit coupling associated with a reduction of the triplet excited-state lifetime.\textsuperscript{39} Therefore, heavy metal complexes with organic luminophores enhance the phosphorescence properties with long lifetimes and high quantum efficiencies, as well as, contribute to the development of light-emitting devices (LEDs) applications.

3.1.2 Palladium Catalyzed Coupling Reaction

There are several coupling reactions of copper (I) acetylenes with haloarenes or
haloalkenes, which include but are not limited to, the Stephans-Castro, the Cassar, and the Heck coupling reactions. Sometimes, their scope is limited by the violent reaction conditions, as well as, by the difficulties in the preparations of cuprous acetylides. Sonogashira has reported that an acetylenic hydrogen is easily substituted by iodoarenes or bromoalkenes with bis(triphenylphosphine)palladium dichloride and cuprous iodide co-catalyst system in diethylamine solvent under a very mild condition. The Sonogashira coupling reaction results in more remarkable results for the synthesis of aryl- or alkenyl- substituted acetylenes.40

The copper co-catalyzed Sonogashira reaction takes place through two independent catalytic cycles (Figure 3.2). For the palladium cycle, the active palladium (0) catalyst, which was prepared by reductive elimination of bis(triphenylphosphine)-palladium dichloride (II), reacts with the aryl halide in an oxidative addition to Pd (II) complex. This complex reacts in a rate limiting transmetallation with the copper acetylide, produced in the copper cycle, expelling the copper halide. Both organic ligands are trans oriented and convert to a cis orientation in a trans-cis isomerization. In the final step the product is released in a reductive elimination with regeneration of Pd (0) catalyst.

For the copper cycle, the employed triethylamine is not basic enough to deprotonate the terminal alkyne. However, the π-complex of the copper halide and alkyne increases the acidity of the alkyne, resulting in easy deprotonation. The copper acetylide reacts with the palladium intermediate and regenerates the copper halide.
3.2. Approach for Conjugated Organic Light Harvesting Materials

The second research project is related to the luminescence properties with polycyclic aromatic hydrocarbons. This project is in collaboration with Dr. Omary’s group on the luminescence properties. Dr. Omary’s group developed the enhancement of the phosphorescence of organic luminophores upon interaction with a mercury trifunctional Lewis acid. As shown in Figure 3.3, the trimeric perfluoro-o-phenylene mercury acts as a Lewis acid, which is an electron poor compound, with electro-withdrawing fluoro substituents. The fluorinated ligands can improve the thermal and oxidative stability, as well as, reduce the concentration quenching of luminescence to metal adducts. The
organic molecules (pyrene, naphthalene, and biphenyl), having structural rigidity, act as Lewis bases, which is an electron rich compound.

![Diagram of organic molecules and metal complexes]

**Figure 3.3.** π-Facial complexation of aromatic substrates to trimeric perfluoro-o-phenylene.

The rigid organic luminophores exhibit greater luminescence quantum yield in the form of the complexation with metal ion because of the inhibition of the internal conversion rates and vibrational motion in the compounds. Based on fundamental acid-base chemistry, the mercury trimer and polycyclic aromatic hydrocarbons interact with each other and form a π-facial complexation of the aromatic substrates to the trimeric perfluoro-o-phenylene mercury, leading to extended binary supramolecules.

The π-stack complexes, exhibiting strong spin-orbit coupling effect in the presence of mercury atoms, allow the phosphorescent emission from the triplet excited state of the aromatic molecule to the singlet ground state. As a result, these π-stack complexes produce excellent room temperature phosphorescence properties with red, green, and
blue light for pyrene-, naphthalene-, and biphenyl- trinuclear mercury complexes by the steady-state and time-resolved photoluminescence measurements in the solid state.\textsuperscript{32}

Based on the development of outstanding electroluminescent materials in previous studies, the approach concerning the trinuclear complexes with diverse aromatic compounds, as alternative luminophores, will significantly contribute to the enhancement of the phosphorescence in optoelectronic device applications as well as control the color and quantum yield of phosphorescent emission.

The primary focus of this research project, in collaboration with Dr.Omary’s research group, is aimed at the preparation of prospective luminescent candidates, which include arene-sensitized phosphors as new emitting materials for organic light-emitting diodes (OLEDs). The arene substrate luminophores possess highly conjugated systems of polycyclic aromatic hydrocarbons connected with ethynyl units. These conjugated compounds consist of polycyclic aromatic hydrocarbons, such as, naphthalene, anthracene, pyrene, and phenanthrene connected via 1,3,5-triethynylbenzene core (Figure 3.4).

Most polycyclic aromatic hydrocarbons usually display strong fluorescent emissions, with very high photoluminescence quantum yields associated with the spin selection rule that indicates same-spin multiplicity for the spin-allowed energy transition. As a result of the spin-allowed energy transition from singlet to singlet, organic fluorophores show somewhat less electroluminescence quantum efficiency. In order to increase optoelectronic properties in organic light-emitting devices (OLEDs), phosphorescent heavy metal organic complexes accompanied with the emission from triplet to singlet states have been increasingly explored.
Figure 3.4. Arene substrate luminophores of polycyclic aromatic hydrocarbons.

The luminophores, shown in Figure 3.4, are expected to enhance the phosphorescence of the organic substrate in the presence of the heavy metal because of spin-orbit coupling. These polycyclic aromatic hydrocarbons are selected to develop superior electroluminescence quantum efficiency with long lifetime and potential for adjustment of the brightness and tunable emission color by varying the organic luminophores. Hence, the desired polycyclic aromatic hydrocarbons are systematically synthesized by Sonogashira coupling reaction, followed by the formation of \( \pi \)-stack
complexes with trimeric perfluoro-o-phenylene mercury as a heavy-atom inducer, to investigate the expected electroluminescent properties.

3.3. Approach for Two and Three-coordinate Gold (I) Complexes

Recently, luminescent monovalent gold (I) complexes have attracted considerable attention in the optoelectronic applications. Owing to the presence of heavy metal atom in the Au (I) complexes, the phosphorescence nature occurs from a metal-centered or metal-to-ligand charge-transfer excitation.42 The most prevalent gold (I) complexes are two-coordinate (AuL₂), three-coordinate (AuL₃), and four-coordinate (AuL₄) species, which can be distinguished based on the presence of gold-based luminescence. While two-coordinate gold complexes have gold-based luminescence in the presence of Au-Au interactions, luminescence in tree-coordinate gold complexes occurs with or without Au-Au interactions. In the case of four-coordinate gold complexes, any Au-based luminescence is not observed.43

Omary’s earlier works have demonstrated that the systematic tuning of the phosphorescence energies, lifetimes, and color is adjusted by controlling steric bulk in three-coordinate Au (I) complexes. Especially, three-coordinate Au (I) mononuclear, binuclear, and polynuclear complexes exhibit Au-centered phosphorescence with large Stoke shifts.44 With extension of ideas of the previous work to conjugated dendrimeric gold (I) complexes, the present Omary’s work has shown the characterizations of the lower lying excited stated of monovalent Au (I) complexes containing arylphosphine ligands, by investigating photophysical and optoelectronical properties. These attractive Au (I) complexes exhibit the spin-orbit coupling in the presence of heavy atom effect.
Moreover, the metal-centered emission is most favorable because of the direct influence of the metal in phosphorescence transitions shortening of triplet life times.\textsuperscript{44}

As shown in Figure 3.5, the organometallic dendrimeric materials possess structural rigidity of alkynyl backbones with the extent of π-delocalization and, hence act as good chromophores with superior luminescence properties.

![Two-coordinate Au (I) complex TEP-PPh\textsubscript{2}AuCl and Three-coordinate Au (I) complex TEP-PPh\textsubscript{2}AuPPh\textsubscript{3}Cl](image)

**Figure 3.5.** Two- and three-coordinate Au (I) complexes.

The transition metal acetylide complexes, having a delocalized π-system, allow communication between coordinated metal centers.\textsuperscript{45} Furthermore, the transition metal complexes, containing acetylene units, stabilize alkyne and vinylidene intermediates and catalyze cross coupling reactions because of the transition metal d orbital interaction with p orbitals of conjugated alkynyl ligands. Therefore, complexes, with electronic delocalization across the transition metal centers linked by σ-bonded triethynylbenzene units, have significant physical, electronic and optical properties compared to conjugated organic compounds.\textsuperscript{46}
Based on the aforementioned studies, we have been exploring luminophores, which possess extended conjugation in dendritic macromolecules, by binding phosphine ligands at the periphery of the 2,3,6,7,10,11-hexaethynyltriphenylene to produce a two- or three-coordinate gold (I) complex (Figure 3.6).

Figure 3.6. TPE-PPh₂AuCl 41 and TPE-PPh₂AuPPh₃Cl 42 complexes.

Compared to the previous two- and three-coordinate gold complexes, TEP-PPh₂AuCl and TEP-PPh₂AuPPh₃Cl, the TPE-PPh₂AuCl and TPE-PPh₂AuPPh₃Cl complexes have a larger conjugated triphenylene core center connected with alkyne groups. Triphenylene has fascinating properties in fluorescence and ultraviolet absorption. Hence, these complexes are expected to show unique luminescent properties in luminescent color, brightness, and lifetimes. The proposed potential luminescent gold (I) complexes can act as good chromophores with enhanced light emission because of the extended conjugation and its structural rigidity. The two- and
three-coordinate gold (I) complexes were constructed by palladium-catalyzed alkynylation of haloarenes with trimethylsilyl acetylene, hydrolysis, introduction of phosphine ligands, followed by metallation with gold complexes.
4.1. Synthesis and Optical Properties

The synthesis of proposed polycyclic aromatic hydrocarbons is shown in Scheme 4.1. The preparation starts from bromonaphthalene 43, which underwent a Sonogashira coupling reaction with ethynyl-trimethylsilane in the presence of a palladium catalyst and copper iodide co-catalyst in triethylamine. Trimethylsilylacetylene (TMSA) is one of the most suitable protected acetylenes because it forms stable, crystalline, TMS-protected intermediates. Mild basic hydrolysis readily removes the TMS group from the trimethylsilyl-protected ethynyl aromatic compounds. As a result of the coupling reaction, 44 was produced in 80% yield. The coupling reaction was followed by hydrolysis with potassium carbonate in methanol/dichloromethane to give 93% of 45.

Scheme 4.1. Synthesis of 1-ethynlnaphthalene 45.

Scheme 4.2 shows the last step involving the coupling reaction between ethynlnaphthalene and tribromobenzene, 46, under palladium catalyst and copper iodide co-catalyst in triethylamine. However, using tribromobenzene, only the mono-, disubstituted compound, and major homocoupling by-product of terminal alkynes was
isolated, instead of the desired tri-substituted compound. The structure of homocoupling dimer was established by X-ray determination.

\[
\begin{align*}
\text{Scheme 4.2.} & \quad \text{Coupling reaction of ethynyl arene compound with tribromobenzene.}
\end{align*}
\]

To avoid this undesired reaction, tribromobenzene was converted into the more reactive triiodobenzene, 50, with potassium iodide, nickel, and iodine in freshly distilled DMF solvent at 185-190 °C (Scheme 4.3).\textsuperscript{47}

\[
\begin{align*}
\text{Scheme 4.3.} & \quad \text{Synthesis of triiodobenzene 50.}
\end{align*}
\]

Triiodobenzene was purified by multiple sublimations, to remove bromoiodobenzene mixtures and impurities, giving white crystalline needles in a 60% isolated yield. The
prepared triiodobenzene was found to undergo tri-alkynylation with ethynylnaphthalene, employing a bis(triphenylphosphine)dichloropalladium and cuprous iodide catalyst as shown in Scheme 4.4. Therefore, a higher yield of the expected tri-substituted conjugated aromatic compounds was obtained.

![Scheme 4.4. Preparation of tri-substituted polycyclic aromatic hydrocarbon 35.](image)

The proposed polycyclic aromatic hydrocarbons, which contain anthracene, pyrene, and phenanthrene moieties, were synthesized in a similar manner to the preparation of compound 35. However, compared to 1,3,5-tris(2-(naphthalen-1-yl)ethynyl)benzene 35, the polycyclic aromatic hydrocarbons possessing anthracene, pyrene, and phenanthrene aromatics were generated with relatively lower yields and several side products, such as, mono- or di-substituted compounds and homocoupling dimer of the terminal alkynes.

We have considered that electron-withdrawing groups, on the aryl halide, reduce the electronic density on C-X bond by the presence of electron-withdrawing groups and activate the C-X bonds toward oxidative addition of Pd (0) catalyst thus facilitate substitution of halo substituents. Whereas electron-donating groups on acetylides
would generate more anionic nucleophiles that should form the corresponding copper acetylide.

Scheme 4.5. Preparation of tri-substituted polycyclic aromatic hydrocarbons 36, 37, 38.

The proposed polycyclic aromatic hydrocarbon substituents, which involve naphthalene, anthracene, pyrene, and phenanthrene, are represented as electron-withdrawing groups by resonance effect. Therefore, the more fused polycyclic aromatic hydrocarbons on acetylides, which have more extensive delocalization of charges, would form relatively a weak anionic nucleophile for the copper acetylide. This would result in a poor yield of tri-substituted polycyclic aromatic hydrocarbons.

UV spectroscopy of the polycyclic aromatic hydrocarbon, 1,3,5-tris(2-(naphthalen-1-yl)ethynyl)benzene 35, showed the maximum wavelength around 280 nm.
in $10^{-3}$ M in CH$_2$Cl$_2$ in 1 cm cuvette. Figure 4.1 shows the luminescence spectroscopy of compound 35 that showed excitation with 320 nm and emission with 430 nm. The luminescence color of 1,3,5-tris(2-(naphthalen-1-yl)ethynyl)benzene 35 was blue. These prepared polycyclic aromatic hydrocarbon compounds will be used to form $\pi$-stack complexes with trimeric perfluoro-o-phenylene mercury for luminescence studies.

![Luminescence spectroscopy of 35.](image)

**Figure 4.1.** Luminescence spectroscopy of 35.

4.2. Gold Complexes

The preparation of two and three coordinate gold complexes, having conjugated organic ligands, is another focus of my luminescence project. The preparation of the proposed two coordinate gold complex is shown in Scheme 4.6.
First, diphenyl phosphorus was attached to the ethynyl proton of 2,3,6,7,10,11-hexaethynyltriphenylene 23, the core molecule for dendrimer 2. Adaptation of a synthetic method by Liu,48 produced 2,3,6,7,10,11-hexakis(2-(diphenylphosphino)ethynyl)triphenylene 60 by treatment of hexaethynyltriphenylene 23 with n-BuLi, followed by addition of Ph₂PCl in THF.49 With the collaboration of Dr. Omary’s research group the final step was carried out, in the preparation of the gold complex, containing prepared organic ligand 60, by metallation. The organic ligand 60 was characterized by ³¹P NMR spectroscopy analysis, which showed a singlet at -33 ppm.

Figure 4.2 shows the UV spectroscopy of the organic ligand, 2,3,6,7,10,11-hexakis(2-(diphenylphosphino)ethynyl)triphenylene 60. The UV spectroscopy showed a maximum wavelength around 416 nm, in 10⁻⁴ M, in chloroform, in 1 cm cuvette.

![UV spectroscopy of 10⁻⁴M C₁₀₂H₆₆P₆ in Chloroform in 1cm Cuvette](image)

**Figure 4.2.** UV spectroscopy of 60.
In Figure 4.3, the luminescence spectroscopy showed the excitation with 380 nm and emission at 500 nm. The luminescence color was light green.

Furthermore, Dr. Omary’s research group will synthesize the proposed three coordinate gold complex 42, TPE-PPh₂AuPPh₃Cl by the introduction of triphenylphosphine ligands on gold metal centers of TPE-PPh₂AuCl complex 41.

![Solid luminescence spectroscopy of 60.](image)

**Figure 4.3.** Solid luminescence spectroscopy of 60.

4.3 Conclusions

In the first project for the synthesis of luminescent materials, the arene substrate luminophores, which possess highly conjugated systems of polycyclic aromatic hydrocarbons connected with a 1,3,5-triethynylbenzene core, were systematically synthesized via palladium catalyzed coupling reaction. The formation of π-stack
supramolecules between prepared organic luminophores and trinuclear mercury complex will be followed to investigate the electroluminescent properties.

The proposed organic luminophores, which were connected with $\sigma$-bonded acetylene units, showed luminescent properties. The conjugated organic ligands showed luminescent properties by determining solid luminescence spectroscopy.

Furthermore, novel organometallic dendrimers, linked by rigid alkynyl backbones with a large extent of conjugated system, can be developed by constructing higher generations on interior metal centers with appropriate schematic design of building blocks, through a stepwise divergent synthetic strategy.

4.4 Experimental

**General Methods.** Unless otherwise stated, all starting materials were purchased from Aldrich Chemical Co. and were used without further purification. All atmosphere sensitive reactions were carried out under nitrogen, over an anhydrous calcium sulfate gas-drying unit. Solvents used, were of reagent grade and purified by standard methods: diethyl ether was distilled over sodium/benzophenone, triethylamine was distilled over calcium hydride, tetrahydrofuran was distilled over potassium/benzophenone, and dimethylformamide was distilled over anhydrous magnesium sulfate. All NMR solvents (CDCl$_3$, with and without TMS) were stored over 4 Å molecular sieves prior to use. Analytical TLC was performed on aluminium backed, pre-coated silica gel plates and visualization was accomplished with UV light. Flash column chromatography was carried out with silica gel (60Å mesh) from 40-63 µm.
NMR spectra were obtained at room temperature with a Varian VXR-500 spectrometer, operating at frequencies of $^1\text{H}$ 499.82 MHz and $^{13}\text{C} \{^1\text{H}\}$ 125.67 MHz, respectively, or a Varian Gemini-200 spectrometer, operating at frequencies of $^1\text{H}$ 200.0 MHz and $^{13}\text{C} \{^1\text{H}\}$ 50.3 MHz, employing a deuterium sample of internal lock unless noted otherwise. The $^1\text{H}$ chemical shifts are reported relative to CHCl$_3$ (7.24 ppm) and $^{13}\text{C} \{^1\text{H}\}$ chemical shifts are reported relative to CDCl$_3$ (77.0 ppm). $^{31}\text{P} \{^1\text{H}\}$ NMR spectra were obtained at room temperature with a Varian Unity 300 spectrometer, operating at frequencies of 121.426 MHz. Reported melting points were obtained with a Mel-Temp capillary apparatus and are uncorrected.

1,3,5-tris(2-(naphthalen-1-yl)ethynyl)benzene (35). A 250 mL two-neck round-bottomed flask was charged with 1,3,5-triiodobenzene 50 (280 mg, 0.614 mmol), Pd$_2$(dba)$_3$ (24.2 mg, 0.0260 mmol), CuI (7.80 mg, 0.0410 mmol), PPh$_3$ (58.5 mg, 0.223 mmol) in triethylamine. The mixture was stirred and then 1-ethynyl-naphthalene 45 (0.350 mL, 2.46 mmol) was added dropwise. The suspension was stirred for one day with reflux. After removal of the solvents in reduced pressure, the product was purified by flash column chromatography eluting with hexanes to give the product (260 mg,
80%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.23 (dd, $J = 7.8$ Hz, 0.7 Hz, 6H), 7.92 (s, 3H), 7.90 (dd, $J = 7.8$ Hz, 0.7 Hz, 3H), 7.68 (m, 6H), 7.47 (m, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 134.3, 132.8, 131.5, 129.3, 128.4, 127.8, 127.2, 126.7, 125.8, 124.3, 121.5, 93.0, 88.6.

1,3,5-tris(2-(anthracen-9-yl)ethynyl)benzene (36). In a 250 mL two-necked round-bottomed flask, 10-ethynylanthracene 53 (1.62 g, 7.99 mmol) and 1,3,5-tribromobenzene (0.763g, 2.42 mmol) were dissolved in 100 mL of dry triethylamine. A mixture of Pd$_2$(dba)$_3$ (95.4 mg, 0.104 mmol), and copper(I) iodide (30.9 mg, 0.162 mmol) and PPh$_3$ (226 mg, 0.862 mmol) was added, and the suspension stirred and refluxed for 3 days. After removal of the solvents in reduced pressure, the product was purified by flash column chromatography eluting with hexanes/ethyl acetate (6:1) to give the product (789 mg, 48%). $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ 8.58 (dd, $J = 7.9$ Hz, $J = 0.7$ Hz, 6H), 8.45 (s, 3H), 8.01 (dd, $J = 7.9$ Hz, $J = 0.7$ Hz, 6H), 7.80 (s, 3H), 7.57 (m, 12H).
1,3,5-Tris(2-(pyren-10-yl)ethynyl)benzene (37). In a 250 mL two-necked round-bottomed flask, 4-ethynylpyrene 56 (434 mg, 1.92 mmol) and 1,3,5-triiodobenzene 50 (250 mg, 0.548 mmol) were dissolved in 10 mL of dry triethylamine. A mixture of Pd(PPh₃)₂Cl₂ (15.4 mg, 0.022 mmol), and copper (I) iodide (6.3 mg, 0.032 mmol) was added, and the suspension stirred and refluxed for 3 days. After removal of the solvent in reduced pressure, the product was purified by flash column chromatography eluting with hexanes/ethyl acetate (6:1) to give the product (222 mg, 54%). ¹H NMR (500 MHz, CDCl₃) δ 8.64 (d, J= 9 Hz, 3H), 8.22 (m, 15H), 8.05 (m, 6H), 8.07 (m, 6H).

1,3,5-Tris(2-(phenanthren-9-yl)ethynyl)benzene (38). In a 250 mL two-necked
round-bottomed flask, 9-ethynylphenanthrene \textbf{59} (310 mg, 1.53 mmol) and 1,3,5-triiodobenzene \textbf{50} (200 mg, 0.438 mmol) were dissolved in 10 mL of dry triethylamine. A mixture of Pd(PPh$_3$)$_2$Cl$_2$ (12 mg, 0.018 mmol) and copper (I) iodide (5.0 mg, 0.026 mmol) was added, and the suspension stirred and refluxed for 3 days. After removal of the solvent under reduced pressure, the product was purified by flash column chromatography eluting with hexanes/ethyl acetate (6:1) to give the product (127 mg, 43%).

\[
\text{Triiodobenzene (50).} \quad 1,3,5-
\text{tribromobenzene (4.40 g, 14.0 mmol), KI (14.00 g, 84.14 mmol), Ni powder (8.00 g), I}_2 \ (20.40 \text{ g}) \text{ and freshly distilled DMF (50 mL) were charged into a 250 mL round-bottomed Schlenk flask. The flask was evacuated on the vacuum line at 0 °C for 15 min. The mixture was refluxed under N}_2 \text{ at 185-190 °C for 3.0 hr. A bluish-green color change was observed while the reaction mixture solidified. After cooling, the solution was poured into a 1000 mL separation funnel and washed with 3% aqueous HCl (200 mL) and CH}_2\text{Cl}_2 \ (200 \text{ mL}) \text{ until all material, except for Ni powder, was transferred into the funnel. The CH}_2\text{Cl}_2 \text{ layer was separated, and the aqueous layer was extracted with CH}_2\text{Cl}_2 \ (2 \times 40 \text{ mL}). The combined CH}_2\text{Cl}_2 \text{ phase was washed with distilled water (3 x 100 mL) and dried over MgSO}_4\text{. The solvent was evaporated, leaving a light-brown crude product (3.80g). This was further purified by sublimation at 60 °C overnight to remove most C}_6\text{H}_3I_2Br and other impurities. The residue was sublimed at}
\]
120 to 140 °C to give 50 as fluffy white crystals (3.78 g, 60% yield) mp 184 °C, 1H NMR (500 MHz, CDCl₃) δ 7.99 (s, 3H).

(2-(anthracen-9-yl)ethynyl)trimethylsilane (52). A round-bottomed flask was charged with 9-bromoanthracene 51 (3.07 g, 11.9 mmol), PdCl₂(PPh₃)₂ (251 mg, 0.358 mmol), CuI (91.0 mg, 0.477 mmol), and Et₃N (100 mL). After bubbling with nitrogen gas for 30 minutes, the trimethylsilyl acetylene (5.06 mL, 35.8 mmol) was added by syringe under a nitrogen atmosphere. The suspension was stirred and refluxed for two days. After removal of the solvents under reduced pressure, the crude mixture was separated by column chromatography on silica gel with hexanes to give the product (2.5 g, 80%). 1H NMR (200 MHz, CDCl₃) δ 8.64 (dd, J = 9.1 Hz, J = 0.7 Hz, 2H), 8.41 (s, 1H), 7.98 (dd, J = 9.1 Hz, J = 0.7 Hz, 2H), 7.57 (m, 4H), 0.45 (s, 9H).

10-ethynylanthracene (53). In a round-bottomed flask, (2-(anthracen-9-yl)ethynyl)trimethylsilane 52 (1.76 g, 6.42 mmol) was dissolved with dichloromethane (32 mL) and methanol (30 mL). Potassium carbonate (53.3 mg, 0.385 mmol) was added
to the mixture. The mixture was filled with nitrogen gas and stirred for 24 hours. The solvent was removed under reduced pressure and the resulting residue vacuum dried. The crude mixture was filtered through a short pad of silica gel eluting with hexanes. Concentration of the filtrate resulted in a viscous brown oil (1.6 g, 93%). $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ 8.68 (dd, $J = 9.1$ Hz, $J = 0.7$ Hz, 2H), 8.39 (s, 1H), 7.98 (dd, $J = 9.1$ Hz, $J = 0.7$ Hz, 2H), 7.57 (m, 4H), 4.02 (s, 1H).

**Trimethyl(2-(pyren-10-yl)ethynyl)silane (55).** A round-bottomed flask was charged with 1-bromopyrene 54 (1.00 g, 4.08 mmol), PdCl$_2$(PPh$_3$)$_2$ (85.9 mg, 0.122 mmol), CuI (31.1 mg, 0.613 mmol), and Et$_3$N (100 mL). After bubbling with nitrogen gas for 30 minutes, the trimethylsilyl acetylene (1.30 mL, 8.97 mmol) was added by syringe under nitrogen atmosphere. The suspension stirred and refluxed for two days. After removal of the solvent under reduced pressure, the crude mixture was separated by column chromatography on silica gel with hexanes to give the product (974 mg, 80%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.58 (d, $J = 9$ Hz, 1H), 8.16 (m, 4H), 8.02 (m, 4H), 0.47 (s, 9H).
4-Ethynylpyrene (56). In a round-bottomed flask, trimethyl(2-(pyren-10-yl)ethynyl)silane 55 (900 mg, 3.02 mmol) was dissolved with dichloromethane (12 mL) and methanol (10 mL). Potassium carbonate (25.0 mg, 0.181 mmol) was added to the mixture. The mixture was filled with nitrogen gas and stirred for 24 hours. The solvent was removed under reduced pressure and the resulting residue vacuum dried. The crude mixture was filtered through a short pad of silica gel eluting with hexanes to give the product (600 mg, 88%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.52 (d, $J = 9$ Hz, 1H), 8.12 (m, 4H), 8.04 (dd, $J = 8.5$ Hz, 0.8 Hz, 2H), 7.97 (m, 2H), 3.55 (s, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 130.5, 128.8, 128.6, 127.7, 126.5, 125.9, 125.8, 125.7, 124.6, 82.8, 78.8.

Trimethyl(2-(phenanthren-9-yl)ethynyl)silane (58). In a 250 mL round-bottomed flask, 9-bromophenanthrene 57 (1.00 g, 3.89 mmol) and trimethylsilylacetylene (1.65 mL, 11.7 mmol) were dissolved in 30 mL of freshly distilled THF and 10 mL of dry triethylamine. A mixture of Pd(PPh$_3$)$_4$ (675 mg, 0.584 mmol) and Cul (88.9 mg, 0.467 mmol) was added, and the suspension stirred for 36 hours at room
temperature in the absence of light. After removal of the solvent under reduced pressure, the residue was suspended in diethyl ether and washed with water, and the organic phase was dried over magnesium sulfate. Removing the solvent and separation by column chromatography on silica gel with hexanes gave the product (897 mg, 84%).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.68 (m, 2H), 8.46 (m, 1H), 8.02 (s, 1H), 7.75 (dd, $J$ = 9.5 Hz, 1.5 Hz, 1H), 7.67 (m, 3H), 7.56 (m, 1H), 0.35 (s, 9H).

9-Ethynylphenanthrene (59). In a round-bottomed flask, trimethyl(2-(phenanthren-9-yl)ethynyl)silane 58 (897 mg, 3.27 mmol) was dissolved with dichloromethane (23 mL), methanol (20 mL). Potassium carbonate (45.2 mg, 0.327 mmol) was added to the mixture. The mixture was filled with nitrogen gas and stirred for 24 hours. The solvent was removed under reduced pressure and the resulting residue vacuum dried. The crude mixture was filtered through a short pad of silica gel eluting with hexanes to give the product (1.93 g, 98%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.66 (m, 2H), 8.46 (d, $J$ = 9.5 Hz, 1H), 8.05 (s, 1H), 7.83 (dd, $J$ = 9.5 Hz, 1.5 Hz, 1H), 7.68 (m, 3H), 7.58 (m, 1H), 3.47 (s, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 132.95, 131.10, 130.97, 130.47, 130.03, 128.61, 127.72, 127.00, 126.97, 126.82, 122.78, 122.63, 118.55, 81.92, 81.66.
2,3,6,7,10,11-Hexakis(2-(diphenylphosphino)ethynyl)triphenylene (60).

$n$-BuLi (2.20 mL, 5.55 mmol) was added dropwise to 2,3,6,7,10,11-hexaethynyltriphenylene 23 (333 mg, 0.896 mmol) in THF (10 mL) at 253 K. The reaction mixture was stirred for 30 minutes, and then Ph$_2$PCI (997 µL, 5.55 mmol) was added. The reaction process was monitored by TLC. The reaction mixture was isolated by column chromatography (hexanes/ethyl acetate = 2:1) to give the product (85 mg, 65%). $^1$H NMR (200 MHz, CDCl$_3$) δ 8.68 (s, 6H), 7.67 (m, 24H), 7.27 (m, 36H). $^{31}$P NMR (121 MHz, CDCl$_3$) δ -33.10 (s).

1,3,5-tris(2-phenylethynyl)benzene (62). 2.5 M $n$-BuLi (0.420 mL, 1.05 mmol) in hexanes was added dropwise to the phenylacetylene (115 mg, 1.05 mmol) solution at
-78 °C. A solution of anhydrous zinc chloride (143 mg, 1.05 mmol) in THF was also added dropwise to produce (phenylethynyl)zinc chloride. To a two-necked round-bottomed flask, 1,3,5-tribromobenzene (100 mg, 0.318 mmol) and Pd(PPh₃)₄ (55 mg, 0.048 mmol) were dissolved in THF, and a solution of prepared (phenylethynyl)zinc chloride was added. The resulting mixture was then slowly warmed to room temperature, followed by stirring and refluxing for 3 days. After 1 N HCl was added, the reaction mixture was extracted with diethyl ether. The combined organic layer was washed with brine and dried over MgSO₄. The solvent was evaporated and the residue was purified by column chromatography eluting with hexanes/ethyl acetate (5:1) to give the product (80 mg, 66%). ¹H NMR (500 MHz, CDCl₃) δ 7.62 (s, 3H), 7.46 (m, 6H), 7.28 (m, 9H). ¹³C NMR (125 MHz, CDCl₃) δ 134.07, 134.03, 131.71, 128.63, 128.43, 124.04, 122.80, 90.51, 87.83.
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