

Chemistry of all-carbon materials: structure and properties



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All-carbon materials have received lots of attention in the past. Carbyne, a new allotrope of carbon, is still in controversy towards its synthesis and property. Combining with the Goroff group's research, this project is to prepare the polymer PIDA (polydiiododiacetylene) as a polyrotaxane complex, encapsulated in a column of macrocyclic hosts. The polyrotaxane structure will prevent aggregation of the PIDA strands, allowing for the complete dehalogenation of the polymer to make carbyne. The proposed route is shown in Scheme 1. 1. PIDA, a precursor of carbyne, can be made from diiodobutadiyne and macrocyclic hosts via topochemical polymerization and host-guest strategy, in which macrocyclic host will self-assemble into column structure and diiodobutadiyne will form halogen bonds with host.

All-carbon materials have been widely investigated because of their potential properties, such as electrical conductivity, thermal conductivity and hardness. They exist in different morphologies with various properties, such as diamond, graphite, carbon nanotube, graphere, fullerene and carbyne .

Diamond, consisting of all sp^3 hybridized carbons, has many unusual properties, such as extreme hardness, high optical transmittance and wide band gap and so on. 1 Because of these potential properties, the synthesis of diamond is of great interest. It can be synthesized through chemical vapor deposition, including hot filament chemical vapor deposition (HFCVD); high frequency plasma-assisted chemical vapor deposition (PACVD); and DC plasma discharge. 1b Graphite is made of sp^2 hybridized carbon. It has a layered honeycomb structure and behaves as a good conductor. 2 Fullerenes exist in different sizes, such as C₆₀, C₇₀ and C₈₂. The C₆₀ fullerene was first reported by Kroto and coworkers. 3 It is an all-carbon polyhedral cage

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molecule with each atom sp^2 hybridized and directly bonded to three neighbors. All valences of carbon atom in the molecule are satisfied by two single bonds and one double bond. Graphene is single atom thick layer of graphite, which can be used in composite material, electric battery and hydrogen storage. 4 Carbon nanotubes usually have cylindrical nanostructure and made of different length-to-diameter ratio. Because of its special electrical, electrochemical and optical properties, carbon nanotubes were widely investigated in electronics, biological and energy application. 5 Carbyne, having all- sp -hybridized carbon, is highly reactive.

Carbyne, an sp hybridized all-carbon chain, is a new allotrope of carbon and has potential special properties as all carbon material, which has attracted considerable interest since discovery back in 1960. Because of its instability, it is less well known than the other carbon allotropes. The investigation of carbyne or carbyne-like structures is still underway while the results are often unclear. Researchers have tried to synthesize carbyne or carbyne-like materials in several ways, such as chemical dehydrohalogenation and electrochemical synthesis. Evsyukov et al. 6 studied dehydrohalogenation of poly (ethylene-alt-chlorotrifluoroethylene)(PE-a-CTFE) to make carbyne. PE-a-CTFE was treated with potassium tert-butoxide in tetrahydrofuran to form a halogen-substituted polyenyne structure with randomly distributed isolated triple bonds. Theoretically, the synthesis was showed below.

Elimination of hydrogen halides was incomplete, which could result from the insufficient strength of the base, sterical hindrances caused by its bulkiness and alternation defects in the original copolymer. Wang and coworkers⁷

claimed to form carbyne-like material via electrochemical method. 1, 1, 2-
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trichloroethylene was dehydrochlorinated with t-buthanolate, which was formed from t-butylalcohol on a Ni cathode in dimethylsulfoxide electrolyte solution under anaerobic conditions. However, this method was not effective because of reactive carbon, oxidation with O₂ and cross-linking of polyynes-like chains. In above reports, no evidence of formation of carbyne is observed and the properties of carbyne remain unrealized.

Recently, polyynes, analogues of carbyne, have been widely investigated to predict the properties of carbyne. Polyynes are one-dimensional chains with alternating single and triple bonds. The synthesis of long polyynes chains was first reported by Walton and coworkers.⁸ They used Cu-catalyzed oxidative Hay coupling techniques to synthesize triethylsilyl-capped polyynes.

Tykwinski and coworkers also synthesized several polyynes with a variety of end groups, in which bulky end groups would increase the stability and solubility of polyynes. In 2010, Tykwinski reported the synthesis of polyynes with as many as 44 sp-carbons.⁹ They used bulky tris(3, 5-di-t-butylphenyl)methyl (Tr) as end groups and stabilize the chain. The synthesis method is shown in Scheme 1.⁴

When the polyynes become larger and larger, the effect on stability of end groups becomes insufficient. In order to overcome this issue, some researchers encapsulated polyynes into macrocycles to form rotaxanes or polyrotaxanes. Sugiyama and coworkers¹⁰ prepared pseudo-rotaxanes and rotaxanes with cyclodextrin simultaneously to stabilize and to solubilize the carbyne chains. Tykwinski and coworkers¹¹ synthesized polyynes rotaxanes

with 4, 6 and 10 triple bonds in length through active copper-templated coupling. Inspired by these cases, I am trying to design a polyrotaxane, allowing for complete dehalogenation of PIDA to make carbyne.

Polydiacetylenes (PDAs), conjugated polymers with alternating double and triple bonds in the backbone, are prepared via topochemical polymerization of aligned diynes. Generally, topochemical polymerizations occur in a condensed phase, in which the monomers are preorganized and the final structures of the product are determined by the preorganization. In 1969, the synthesis of PDA was first described by Wegner,¹² introducing the 1, 4-polymerization of monomers. In addition, Baughman demonstrated how 1, 4-polymerization of diynes works and reported necessary parameters for the 1, 4-polymerization.¹³ The monomers are held in alignment. The distance between adjacent monomers is near 5 Å. The intermolecular distance of reacting carbons (C4 and C1') is close to 3.5 Å, which is close to the van der Waals radius of carbon. The tilt angle between monomer diyne and the vertical translation axis should be 45°. Ideal 1, 4-polymerization of diynes is showed below.

Host-guest strategy is used to describe how monomers are aligned for polymerization. Different molecules or ions are held together by some forces to form complexes. In order for topochemical polymerization, monomers should be aligned to meet the geometric requirements. However, some monomers cannot form the right geometry required to polymerize. Host-guest strategy is applied to adjust the monomers to meet the requirements reported by Baughman. Here, hydrogen bonding and halogen bonding work in 1, 4-polymerization through host-guest strategy. Recently, Fowler and <https://assignbuster.com/chemistry-of-all-carbon-materials-structure-and-properties/>

Lauher developed different kinds of diyne monomers to undergo 1, 4-polymerization using the host-guest strategy. In this way, the diyne monomers played the role of guests, which then formed hydrogen bonds with host molecules. The host molecules possessing oxalamides and ureas self-assembled into a structure via hydrogen bonding. Because of hydrogen bonding interactions, the diyne monomers were aligned in proper geometry for 1, 4-polymerization. The following is an example of host-guest strategy for one diyne. ¹⁴ In the cocrystals, the oxalamide host molecule was organized through hydrogen bond with a repeat distance of 4.97 Å. The nicotinyl ester groups of the diyne guest monomers form strong pyridine-carboxylic acid hydrogen bonds to the host molecules.

In addition to Fowler and Lauher' work, the Goroff group also showed halogen bonding interaction could be applied for 1, 4-polymerization with the host-guest strategy. sp^2 and sp hybridized carbon is more electronegative than iodine. Iodoalkynes behaves as Lewis acids and form halogen bonds with Lewis bases, such as pyridine and nitriles. The following is an example of host-guest strategy for diiodobutadiyne (figure 1.3). ¹⁵ In this case, diiodobutadiyne played the role of guest. The hosts with oxalamide group were also organized through hydrogen bonds and designed to align diiodobutadiyne in the right geometry for 1, 4-topochemical polymerization. The repeat distance of diyne monomers was 5.11 Å. The tilt angle was 51°.

Halogen bonds (XBs) is a non-covalent interaction which consists of halogen atom and other neutral atom or anions. The general structure of halogen bonds is showed in Figure 1.4. ¹⁶ In this structure, X is halogen atom, which accepts electron density. It can be Lewis acid and halogen bond donor. D is <https://assignbuster.com/chemistry-of-all-carbon-materials-structure-and-properties/>

the one donate electron density, which behaves as Lewis base and halogen bond acceptor. Y is a carbon, nitrogen, or halogen atom.

The investigation of XB has been continuing for near 200 years. In 1863, the first report on the ability of halogen atoms to form well-defined adducts with electron donor species was described by Frederick Guthrie.¹⁷ In his experiment, I₂ was added to saturated ammonium salt (nitrate or carbonate) and a diiodine/ ammonia system NH₃•I₂ formed. After exposed to air, it decomposes spontaneously into ammonia and iodine, without permanent gas being evolved. After that, halogen bonds became widely investigated. H. A. Benesi and J. H. Hildebrand identified the iodine-benzene complex through UV-vis spectra in 1948.¹⁸ In 1954, Hassel's group used X-ray to show the structure of bromine 1, 4-dioxane.¹⁹ The experiment showed there was a short intermolecular interaction between the oxygen atoms of dioxane and bromine atoms. The interaction was halogen bond. The distance of O–Br bond was just 2.71 Å, which indicated a strong interaction between the bromine and oxygen atoms.

Pierangleo Metrangolo and Giuseppe Resnati, whose research focused on halogen bonds, summarized the characteristic of halogen bonds and their interaction.^{16, 20} Polarizability increases when you move down the periodic table from fluorine atom to the iodine atom. This makes Cl, Br and I have the positive potential charge, which is showed in Figure 1.5. When the halogen atom is attached to an electron-withdrawing group, the positively polarized area will increase. On the one hand, the halogen atom can be the acceptor of electron density. On the other hand, the positive charge locates at sphere's end, which is surrounded by electron neutral ring and negative charge belt.

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Because of the special location of positive charge, the angle of covalent bond and noncovalent bond around halogen atom in $D \cdots X-Y$ is near 180° . This is consistent with research results. Hongjian Jin et al. 21 used diiodobutadiyne and bis(pyridyl)oxalamides to make cocrystal, which was based on halogen bonds between pyridine group's nitrogen and iodine. Polymerization of cocrystal was induced under 3.5 GPa pressure. Although the $N \cdots I-C$ angle changed after polymerization, both angles were still near 180° . They were 169.7° and 161.4° . Investigation of halogen bonds examples in the Cambridge Structure Database is also shown.

Metrangolo and Resnati^{16, 20} showed that halogen bond was relative stronger than hydrogen bond. However, a halogen is larger and more polarizable than hydrogen and halogen bonds are more sensitive to steric hindrance than hydrogen bonds. Halogen atom, electron acceptor in XBs, has some general characteristics. Among the four halogen atoms, the order for forming strong halogen bonding is $I > Br > Cl > F$. The more electron withdrawing atom is, the stronger is the halogen bonds. As to halocarbons, the strength order for halogen bonding is $C-X (sp) > C-X (sp^2) > C-X (sp^3)$. If the halocarbons are unfunctionalized monohaloalkanes, no halogen bonds are observed. Diiodobutadiyne, in which the C is sp hybridized, is a good Lewis acid. 22 The Goroff group used diiodobutadiyne as a guest to make poly (diiododiacetylene) (PIDA) with several hosts.

Self-assembly of macrocycles

Supramolecular chemistry is a rapidly growing field, emphasizing on assembly of discrete molecules. Traditional chemistry deals with covalent

interaction while supramolecular chemistry focuses more on noncovalent interactions, such as hydrogen bonding²³, van der Waals forces²⁴ and π - π interactions²⁵. Self-assembly, a main process involved in supramolecular chemistry, will take advantage of these noncovalent interactions to organize discrete molecules into high order structures. Macrocycles, which have cyclic structures with other functional groups, can be self-assembled in a specific manner to form high order structures. Here I will introduce the self-assembly of macrocycles through hydrogen bonding and π - π interactions.

π - π interactions, well known noncovalent intermolecular interactions, play important roles in self-assembly of macrocycles. The arrangement of aromatic rings has following geometries, such as face-to-face, edge-to-face and slipped stack. Hill and coworkers²⁶ synthesized amphiphilic hexa-peri-hexabenzocoronene, self-assembling via π - π stacking to form a discrete nanotubular object. The object has a uniform and 14-nanometer-wide hollow space. Lauher and coworkers²⁷ also took advantage of π - π stacking to design a tubular macrocyclic polymer. The monomer structure and route to a tubular polymer are shown in Figure 1. 7. The diacetylene-based macrocycles self-assembled into polymerizable slipped π - π stack and polymerized via slow annealing. The macrocycle had two different crystalline forms, which were monoclinic and triclinic form, respectively. After slow annealing at 40 °C, the triclinic forms appeared to undergo crystal-to-crystal polymerization.

Hydrogen bond is an attraction force involves a hydrogen and strong electronegative atom, such as oxygen, nitrogen and fluorine. The

electronegative atoms behave as hydrogen bond acceptor and hydrogen is
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hydrogen bond donor. 28 Macrocyclic peptides and ureas can form high order tubular structures via hydrogen bonds. Ghadiri and coworkers²⁹ used cyclo[-(L-Gln-D-Ala-L-Glu-D-Ala)₂-] to self-assemble into hollow tubes via amide hydrogen bonds. Shimizu and coworkers³⁰ also took advantage of amide hydrogen bond to organize diacetylene macrocycles for topochemical polymerization. In addition, Shimizu and coworkers used macrocyclic bis-ureas to self-assemble into columnar structures through urea hydrogen bonds. In the structure of macrocyclic bis-ureas, two hydrogen atoms in NH group are hydrogen bond donors and the carbonyl groups are hydrogen bond acceptors. The structures of the macrocyclic ureas are shown in figure 1. 8. In 2001, they used bis-urea macrocycles with m-xylene to form the self-assembly tubular structures. 31 The m-xylene kept the macrocycles rigid. However, this macrocycle formed intramolecular hydrogen bonds. Another bis-urea macrocycle with m-phenylether avoided forming intramolecular hydrogen bonds and organized into tubular structures with ordered acetic acid dimer filling inside as guest. The columns were stabilized by hydrogen bonding as well as π - π staking interactions of phenylether.

Except ureas, oxalamides are also used to form hydrogen bonding networks (figure 1. 8). The repeat distances are 4. 6 Å and 5. 0 Å, respectively. 33 Inspired by above work, we plan to design a macrocycle with pyridine, alkyne and oxalamide segments. Pyridine and alkyne segments provide beneficial rigidity, helping the macrocycles cocrystallize with diiodobutadiyne through halogen bonds. oxalamide segments are used for forming hydrogen bonding networks.