Technische Universität München
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Functionalization of Silicon Nanocrystals with Extended Conjugative Systems and Thermoelectric Applications

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Contents

Abstract

Silicon nanocrystals are a remarkably valuable quasi-zero-dimensional semiconductor nanomaterial that has attracted the interest of many researchers because of its unique electro-optical properties, as well as its non-toxic, non-hazardous, low-cost and biocompatible nature. Silicon nanocrystals show a bright future for a wide range of applications, including sensors, LEDs, biomarkers, solar cells, optoelectronic devices, etc. In an attempt to enrich the surface ligands and applications of silicon nanoparticles, this research thesis investigates the following works:

Firstly, a series of terminal alkyne conjugate groups were synthesized and characterized by Sonogashira coupling reactions, which extended the range of surface ligands. Subsequently, in the presence of organolithium reagents, the alkyne-terminated conjugated groups were grafted onto the surface of the silicon nanocrystals. Through a two-steps modification method, both the alkyne-terminated conjugate group and the dodecyl chain can be successfully immobilized onto the particle surface. Red-shifting of the photoluminescence still occurs, especially with silicon nanocrystals modified with the phenylethynyl systems.

Boron-doped silicon nanocrystals were positively synthesized and Raman spectroscopy revealed the presence of boron. The nanomaterials were doped with a PEDOT:PSS conducting polymer and the measured Seebeck coefficients increased significantly (about 36 V/K), by 50% growth compared to the original material, and the doped polymer films were not disrupted.

Zusammenfassung

Silizium-Nanokristalle sind ein bemerkenswert wertvolles quasi-nulldimensionales Halbleiter-Nanomaterial, das aufgrund seiner einzigartigen elektro-optischen Eigenschaften sowie seiner ungiftigen, ungefährlichen, kostengünstigen und biokompatiblen Beschaffenheit das Interesse vieler Forscher geweckt hat. Silizium-Nanokristalle haben eine glänzende Zukunft für ein breites Spektrum von Anwendungen, darunter Sensoren, LEDs, Biomarker, Solarzellen, optoelektronische Geräte usw. In einem Versuch, die Oberflächenliganden und Anwendungen von Silizium-nanokristalle zu bereichern, werden in dieser Forschungsarbeit die folgenden Arbeiten durchgeführt:

Zunächst wurde eine Reihe von endständigen Alkin-Konjugatgruppen synthetisiert und durch Sonogashira-Kopplungsreaktionen charakterisiert, wodurch die Palette der Oberflächenliganden erweitert wurde. Anschließend wurden die Alkin-terminierten konjugierten Gruppen in Gegenwart von Organolithium-Reagenzien auf die Oberfläche der Silizium-Nanokristalle aufgepfropft. Durch eine zweistufige Modifizierungsmethode können sowohl die Alkin-terminierte konjugierte Gruppe als auch die Dodecylkette erfolgreich auf der Partikeloberfläche immobilisiert werden. Eine Rotverschiebung der Photolumineszenz tritt immer noch auf, insbesondere bei Silizium-Nanokristalle, die mit den Phenylethinylsystemen modifiziert wurden.

Mit Bor dotierte Silizium-Nanokristalle wurden positiv synthetisiert, und die Raman-Spektroskopie zeigte das Vorhandensein von Bor. Die Nanomaterialien wurden mit einem leitenden PEDOT:PSS-Polymer dotiert, und die gemessenen Seebeck-Koeffizienten stiegen deutlich an (etwa 36 V/K), und zwar um 50 % im Vergleich zum ursprünglichen Material, wobei die dotierten Polymerfilme nicht gestört wurden.

Table of Abbreviations

AIBN	Azobisisobutyronitrile
ET-1	2-ethynylthiophene
ET-2	1-(thiophenethynyl)-4-ethynylthiophene
ET-3	2-ethynyl-5-((5-(thiophen-2-ylethynyl)thiophen-2-yl)ethynyl)thiophene
FTIR	Fourier transform infrared
FWHM	Full-width at half maximum
GIWAXS	Grazing-incidence wide-angle X-ray scattering
HF	Hydrofluoric acid
HSQ	Hydrogen silsesquioxane
IR	Infrared
LDA	Lithium diisopropylamide
LED	Light emitting diode
MBS	Multicolor molecular beacon
nm	nanometer
PE1	Phenylacetylene
PE2	1-ethynyl-4-(phenylethynyl)benzene
PE3	4-(2-(4-ethynylphenyl)-ethynyl)-1-(2-phenylethynyl)benzene
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonate)
PL	Photoluminescence
SiNCs	Silicon nanocrystals
TGA	Thermogravimetric analysis
UV/VIS	Ultraviolet/visible

List of Publication

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1. Introduction

In 1859, the American Physical Society held a lecture in which Nobel laureate and physicist Feynman proposed the concept of nanotechnology and predicted that humans could utilize single molecules or atoms to assemble the materials as they desired[1]. Since the last century, nanotechnology has been attracting attention from all circles because of its unique significance. In 1982, the tunneling scanning microscope was introduced, and mankind gradually saw the real appearance of the nano world and achieved the observation of the microscopic world of atoms and molecules, and since then nanotechnology has advanced rapidly[2]. Combined with modern science, nanotechnology is deployed in various aspects such as energy and environment, biomedicine, fine chemicals, computer, and electronics technology[3].

Nanomaterials are broadly defined as materials in three dimensions, with at least one-dimensional structural unit in the nanoscale and geometric scales falling in the range of 1-100 nm, or as materials or particles with special properties that treat them as basic building blocks[4]. When the geometric scale of a material is reduced to the nanometer level, the number of active atoms on the surface of the material increases to a large extent in proportion to the number of stable atoms inside, and the physical and chemical properties of the material change significantly, exhibiting special properties that distinguish it from macroscopic matter, such as surface effects, quantum size effects, macroscopic quantum tunneling effects, and small size effects[5]. Therefore, nanomaterials are extensively applied in the fields of national defense science and technology, environmental remediation, and biomedicine[6].

Synthesizing the research progress in recent years, nanomaterials have emerged in various research fields, such as magnetic nanoparticles, carbon nanotubes, quantum dots, carbon dots, nano gold/silver/copper, etc. Fluorescent nanomaterials with both nano-effect properties and good fluorescence performance offer more opportunities in the fields of optoelectronic devices, clinical diagnostics, life sciences, etc[7]. As a new type of nanomaterial with unique optical, electronic, mechanical properties and biocompatibility, silicon nanoparticles are attracting more attention in the direction of electronic devices and sensing[8]. Silicon nanoparticles have more potential applications as they are environmentally friendly and the surface can be easily modified, together with the special properties such as lipophilicity/hydrophilicity of the functional groups on the surface[9].

2. Background and Methods

2.1 Silicon Nanocrystals

The element silicon plays an important role in nature and human society[10]. As the second most abundant element in the earth's crust, silicon-based materials occupy half of the development of the modern semiconductor industry. Materials prepared using silicon are gradually becoming the dominant semiconductor materials with their excellent semiconductor properties and mechanical properties, and dominate the current electronics application industry[11]. Currently, silicon nanotechnology as a more important branch of nanotechnology is becoming a research hotspot in many fields, and this development trend has also promoted the research of many silicon-related materials in practical applications[12].

Silicon nanomaterials are favored by many researchers as a typical representative of zero-dimensional silicon nanomaterials. Since the early 1990s, when porous silicon was first discovered to have a certain degree of luminescence, silicon nanomaterials have received a lot of attention in the field of nanomaterials[13]. Compared with conventional quantum dots, silicon nanomaterials are simple in composition and free from heavy metal elements. As the geometry of silicon nanomaterials shrinks to the intrinsic Bohr radius of silicon (~4.2 nm), silicon nanomaterials exhibit characteristic photoluminescence based on quantum-limited effects, and thus silicon nanomaterials, especially the particles can be treated as a type of quantum dot[14]. With the discovery of quantum confinement effect and quantum tunneling effect, the properties of silicon nanomaterials have been gradually explored[15]. The traditional standard-composition quantum dots, are usually composed of heavy-metal elements (typically CdSe and ZnS)[16], might be prohibited wide-scale use because of the toxicity. Silicon nanomaterials have more advantages compared with the traditional cadmium elemental series and lead elemental series nanoparticles[17], such as: abundant material reserve, low price, green and low toxicity, good biocompatibility, etc. Therefore, they are used in various fields[18], for example LED optoelectronic device, sensor, solar cells, and so on as described below.

In 1990, Canham's research team synthesized mesoporous silicon nanomaterials employing electrolysis of silicon wafers, and room temperature photoluminescence was observed. The phenomenon was later demonstrated to generate nanoscale single crystals of silicon during electrolysis, which resulted in photoluminescence[19]. The particle size of silicon nanoparticles is around 10 nm and has a good quantum size confinement effect, so the photovoltaic properties can be greatly enhanced and the nanoparticles exhibit strong fluorescence[14a, 20]. Thus, the desire to obtain light energy from nanomaterials was envisioned to be realized. In addition, in contrast to conventional semiconductor nanomaterials formed based on elements such as cadmium and lead, silicon nanoparticles also have superior photostability. More importantly, silicon nanoparticles are low toxicity materials that can be used as markers in the human body, where they are degraded to silicic acid through a series of biochemical reactions and eventually cleared through the internal circulation system[21]. Sensors play an important role in environmental protection and monitoring[22], disease prevention and control[23], food industry[24], and other fields. Both optical sensors and electrochemical sensors occupy important branches, while fluorescent sensors, as a kind of optical sensors, possess the advantages of low fabrication cost, low equipment requirements, high sensitivity and short response time[25]. Combining the unique optical properties of silicon nanoparticles with good biocompatibility, a high-performance fluorescent sensor can be designed, such as the detection of catechol and hydroquinone[26]. Through years of development, researchers have conducted in-depth research on the synthesis methods and properties of silicon nanoparticles for applications, and have obtained extensive results. This section will review the common preparation methods, physical and chemical properties, and application progress of silicon nanocrystals.

2.2 Synthesis of Silicon Nanocrystals

Since the discovery of silicon nanomaterials in the 1990s, after years of research and development, a variety of mature preparation techniques have been developed to prepare silicon nanocrystals with different properties, which can be generally summarized as bottom-up and top-down approaches.

2.2.1 Bottom-up Preparation Approach

In the "bottom-up" preparation method, atoms are rearranged and self-assembled to form slightly larger silicon nanomaterials[27]. Small silicon-based molecules are usually treated as precursors for the reaction, which are reduced and form silicon nanoparticles through a self-assembly process. Currently, the three most used “bottom-up” approaches are the microemulsion, hydrothermal, and liquid phase reduction methods, which are described in more detail below.

Microemulsion method

Typically, silicon tetrachloride or organo-silane is the raw material for this method, and the silica nanoparticles are prepared by chemical process by utilizing the modulating effect of surfactants. A facile one-pot reverse microemulsion process is studied to produce Ag@SiO_2 core-shell nanoparticles (Fig.2-1)[28]. In the same microemulsion, the reaction included the synthesis of silver nanoparticles, in situ silica coating, and Eu^{3+} chelate-doped silica shells[28]. Thus, this method is relatively fast and simple to perform.

The product obtained by this method has a relatively regular crystal shape and controlled particle size, and has strong luminescent emissions properties[28]. Further, modification by surface functionalization with different functional groups improves chemical properties of nanoparticles[29].

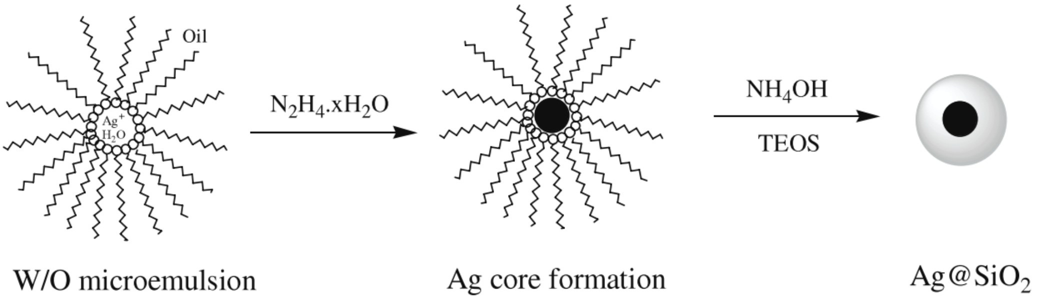


Fig.2-1 Preparation of Ag doped silicon nanoparticles[28]. Reprinted from ref. 28 with permission.

The silicon nanoparticles prepared by the microemulsion method have the following advantages: uniform particle size, good monodispersity, strong and stable fluorescence, but the disadvantages of this method are the cumbersome reaction process, high requirements for the reactants, low yield of the resulting silicon nanoparticles, and uneven quality.

Hydrothermal method

After years of research, many scientists have prepared silicon nanoparticles with excellent water solubility and monodispersity in size using hydrothermal methods[30]. For example, redox reactions occur under microwave radiation. $C_6H_{17}NO_3Si$ molecules are easily reduced by trisodium citrate ($C_6H_5Na_3O_7$ as reduction reagent), and the reaction continues until the concentration of $C_6H_{17}NO_3Si$ molecules reaches a critical value, when the nucleation stops (Fig.2-2)[31]. This is followed by the Ostwald ripening stage. Small nanocrystals have a relatively large specific surface group, but this also leads to chemical instability, so larger size and more stability particles are formed.

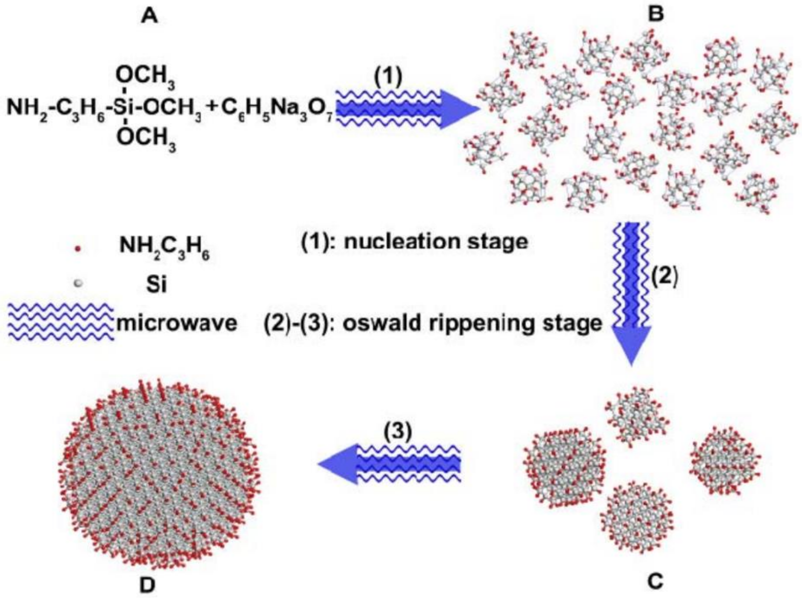


Fig.2-2 Schematic illustration of synthesis of SiNPs. (A) reaction precursor; (B) nuclei; (C) small size nanocrystals; (D) large size nanocrystals[31]. Adapted with permission from ref. 31. Copyright 2013 American Chemical Society.

The raw material 3-aminopropyltriethoxysilane and the reducing agent trisodium citrate dihydrate were added to anaerobic water, and the mixed solution was transferred to a polytetrafluoroethylene reactor, after the reaction water-soluble silica nanoparticles were obtained[32]. Winnik et al. also used 3-aminopropyltriethoxysilane as a raw material and added silicon tetrabromide to obtain silica nanoparticles with particle sizes between 1-2 nm which emit blue light in water under UV-irradiation. The measured quantum yield of this material is approximately 34%[33]. In addition, the hydrothermal method also includes the compounding of 3-aminopropyltriethoxysilane/ascorbic acid[34] or N-[3-(Trimethoxysilyl)propyl]ethylenediamine/catechol[35] as reaction precursors, both of which lead to silica nanoparticles with excellent optical properties. The preparation of SiNPs by hydrothermal method has the advantages of good water solubility, small size, strong fluorescence and large amount of synthesis, but at the same time, this method is time-consuming, and the reaction conditions and equipment requirements are more demanding.

Liquid phase reduction method

Cheng et al. describe a method for the synthesis of silica nanoparticles in toluene solution[36]. Allyl trichlorosilane, as the reactants and surfactants, self-assemble around a halogenated silane precursor. SiX_4 core and allyl trichlorosilanes reverse micelle are formed, subsequent treatment with $LiAlH_4$, surface-functionalized silicon nanoparticles are synthesized (Fig.2-3). The chlorine-modified silicon nanoparticles were very unstable during this process, so the researchers treated silicon tetrachloride/allyltrichlorosilane with $LiAlH_4$ to obtain silicon nanoparticles modified with olefin groups that could be further functionalized[36].

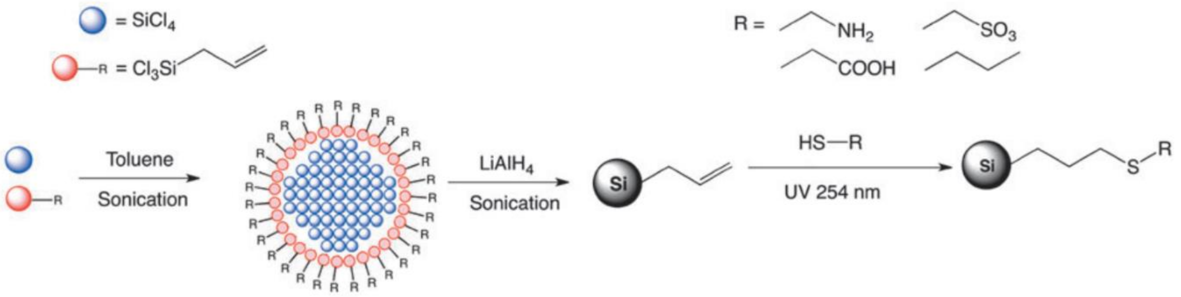


Fig.2-3 One-pot synthesis of alkene coated SiNCs and further functionalization via thiol–ene click chemistry[36]. Adopted from ref. 36 with permission from The Royal Society of Chemistry.

The reducing agent of this method affects the formation of silicon nanoparticles, but the preparation method is relatively simple[37]. The silicon tetrachloride and the reducing agent Zintl salt underwent a substitution reaction to obtain silicon nanoparticles with the surface modified by chlorine, followed by the addition of metal-organic reagents to complete the surface modification of silicon nanoparticles[38].

Although important progress has been made in the preparation of SiNCs using the solution reduction method[39], the current method still has some drawbacks, firstly, the surface of SiNCs prepared using this method is filled with Si-H bonds, which leads to poor water solubility and stability of SiNCs, and thus requires further silanisation. The catalyst can easily adhere to the surface of Si quantum dots, which increases the biotoxicity of the prepared products, and the modification by silanisation also increases the production cost.

2.2.2 Top-down Preparation Approach

The top-down preparation method obtains small-sized silicon nanomaterials from bulk materials utilizing physical or chemical methods such as grinding, fragmentation, and etching[40].

Mechanical grinding method

High-energy consumption is used to refine bulk silicon materials to the nanometer scale by mechanical grinding. Silicon nanoparticles are obtained with this method[41]. Therefore, millimeter-sized monocrystalline silicon wafers are used as starting material. These are placed in a high-energy ball mill protected by inert gas, and organic molecules such as unsaturated hydrocarbons are added to passivate the surface of silicon starting material[42]. Under the continuous impact and collision of the steel balls in the high-energy ball mill, the size of the single-crystal silicon wafers is continuously reduced and new reactive interfaces are formed on their surfaces. The highly reactive sites at the interface can directly interact with the unsaturated bonds of hydrocarbon organic molecules and form stable Si-C bonds. After high-energy ball milling, the size of the particles is sharply reduced to the nano-sized level. The functionalized particles can be dissolved in 1-octyne solution, while the less reactive large-sized particles are precipitated and thus separated (Fig.2-4)[43].

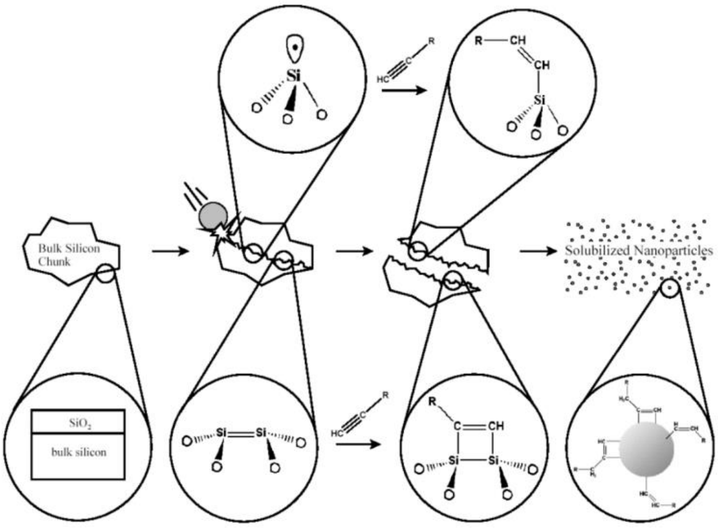


Fig.2-4 Preparation of functionalized silicon nanoparticles by mechanical grinding[43]. Reprinted from ref. 43 with permission.

This is a common technique of reducing the size of materials. The fluorescence emission wavelength of silicon nanoparticles obtained by this method is in the blue wavelength band, and the silicon nanoparticles are relatively stable[43-44]. This method is overly demanding in terms of preparation apparatus and requires high energy demanding, so mechanical grinding is rarely used to prepare silicon nanoparticles at present.

Ultrasonic treatment method

Hwang et al. used ultrasonic treatment of electrochemically etched porous silicon to obtain polydisperse colloidal solutions of silicon nanoparticles with an average particle size of about 5 nm (Fig.2-5). As prepared silicon nanoparticles were re-etched in HF/HNO_3 solutions with different composition ratios to obtain silicon nanoparticles with different sizes, luminescence intensities, and quantum yields (Fig.2-5)[45].

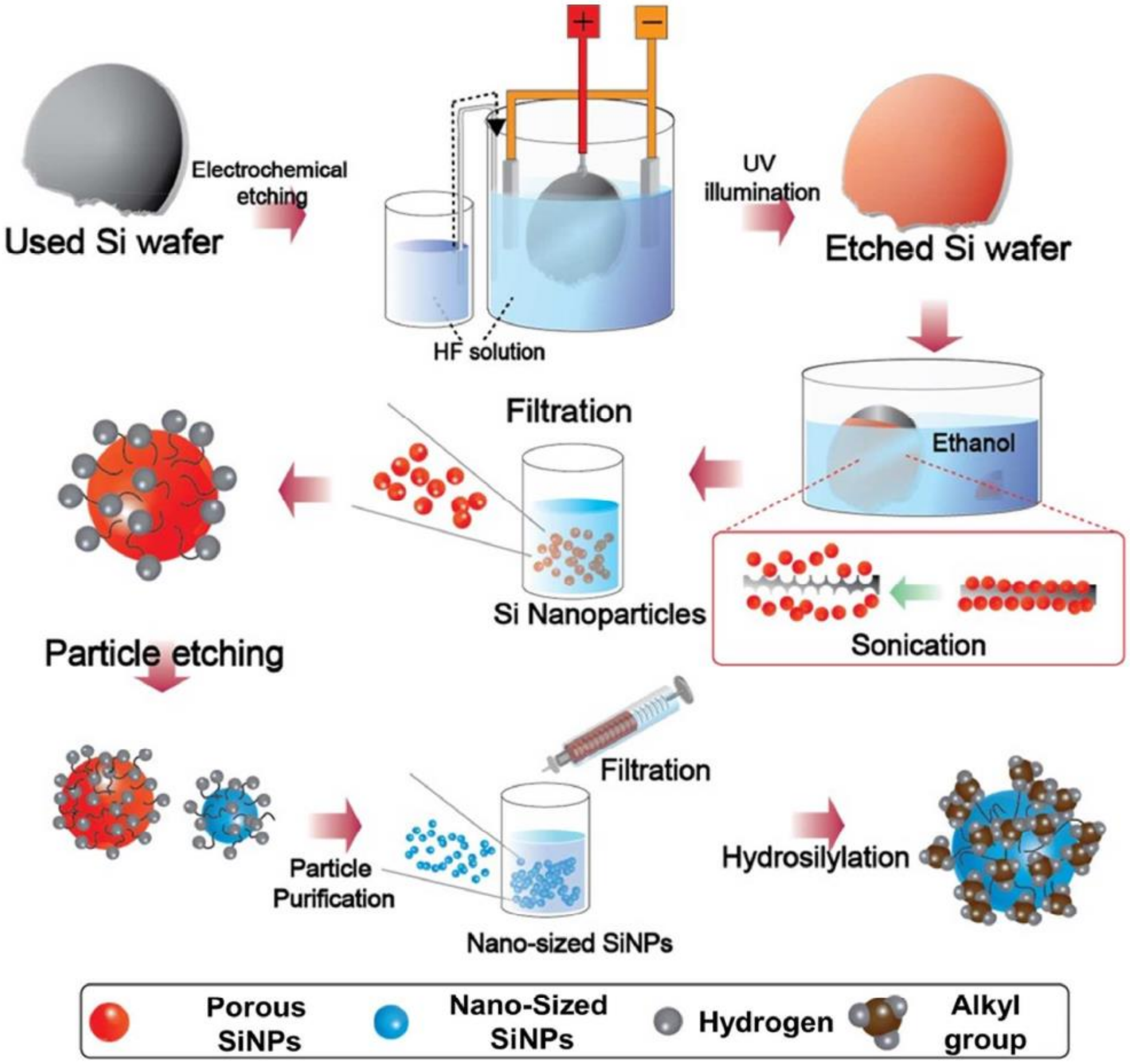


Fig.2-5 Schematic diagram of silicon nanoparticle preparation by ultrasonic method[45]. Adapted with permission from ref. 45. Copyright 2015 American Chemical Society.

Laser ablation method

Laser ablation, also known as laser deposition and laser evaporation, is employed to prepare small-sized silicon nanoparticles[46]. Currently it is a classical physical method more frequently used by researchers. A high-energy laser beam irradiates the surface of the bulk silicon material. After the material surface absorbs the laser radiation energy, the electromagnetic energy is converted into electronic excitation energy, which is subsequently converted into thermal, chemical, and mechanical energy. In consequence, the silicon material is rapidly heated, melted and evaporated. The mixture formed during the evaporation process is then cooled and crystallized to produce a certain amount of silicon nanoparticles[47]. In the past decade of scientific and technological development, the mechanism of laser ablation has been more thoroughly studied and the preparation method has been continuously improved. In the presence of low-pressure inert gas, researchers have been able to prepare silicon nanoparticles with adjustable fluorescence ranges and different sizes[48]. The advantages of the laser ablation method are the rapid reaction and the purity of the product, the small size and water solubility of the obtained silicon nanoparticles, and their excellent stability. However, the disadvantage of this method is the extremely low yield of the product, so it is only suitable for studying the photoluminescence mechanism, crystallinity and other characteristics in the laboratory.

Etching method

In this preparation method, large-size silicon materials are etched by a chemical etching solution[49]. The advantages of this method are the mild preparation conditions and the simplicity of the operation.

As early as 1994, Henglein et al. used HF etching of suspended silicon, followed by employing a cyclohexane-propanol ($V_{cyclohexane} : V_{propanol} = 1:1$) mixture to functionalize the above products, resulting in silicon nanoparticles with orange and red fluorescence emission[50]. In 2004, Swihart et al. used laser-induced pyrolysis of silane to obtain larger size silicon nanoparticles, which were subsequently etched with a HF/HNO_3 solution and finally they successfully prepared silicon nanoparticles with a particle size of about 5 nm[51].

Using hydrogenated silicon nanoparticles with a particle size of 3 nm as raw material, and ethanol (EtOH)/H_2O_2 solution as etching solution, Kang et al. successfully synthesized silicon nanoparticles with good water solubility (Fig.2-6 a)[52]. The fluorescence emission wavelength and particle size of silicon nanoparticles, depend on each other, so the emission color changes according to the particle size. To regulate the particle size of silicon nanoparticles and thus tune their fluorescence behavior, the researchers controlled the oxidation in the etching solution (different etching time, 0.5 - 24 hours). Finally, they obtained silicon nanoparticles with different fluorescence emission wavelengths (Fig.2-6 b and c).

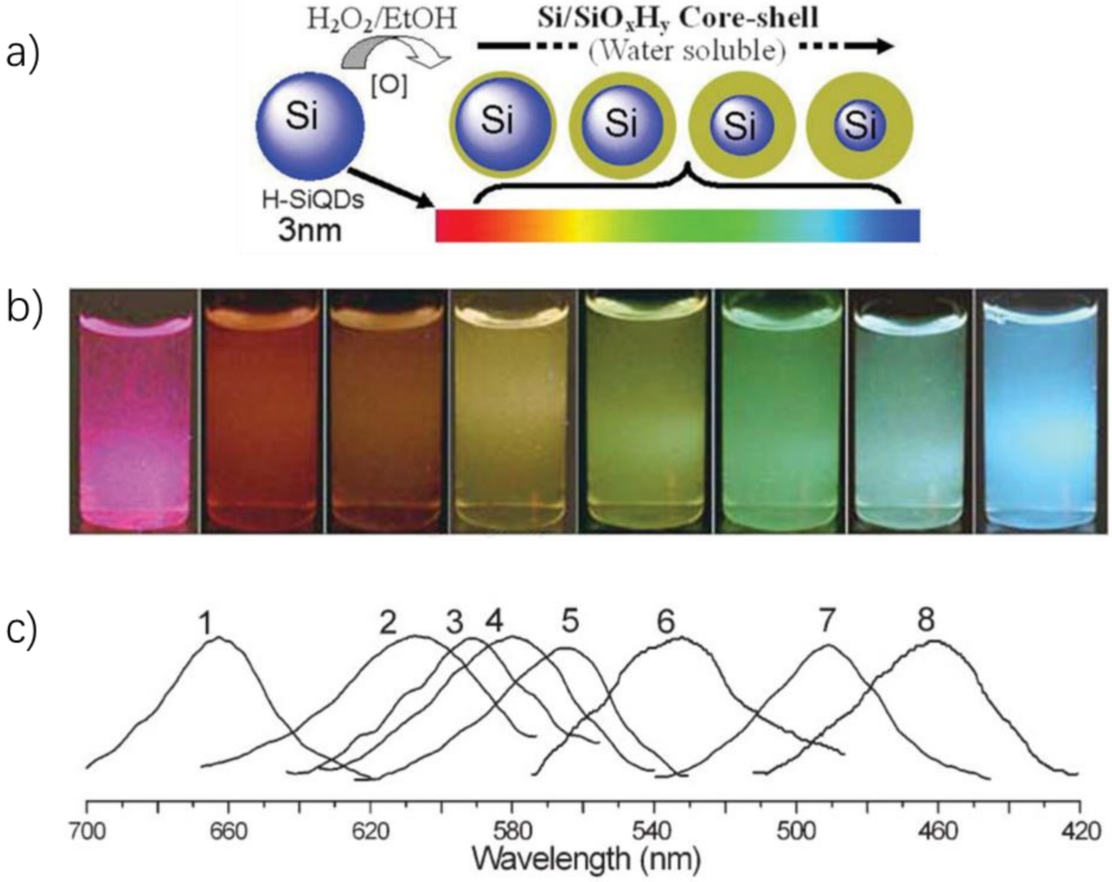


Fig.2-6 a) Schematic of SiNCs obtained by EtOH/H_2O_2; b) Photographs of H-SiNCs (left, red emission) and water-soluble SiNCs; c) PL spectra of H-SiNCs and SiNCs after oxidization[52]. Reprinted from ref. 52 with permission.

Veinot et al. proposed an improved method to prepare freestanding silicon nanoparticles by the following formulation: HSQ was first heated to a certain temperature (500 °C – 1000 °C) in a 4% H_2 and 96% N_2 atmosphere, and then etched with a HF/H_2O/EtOH solution, finally silicon nanoparticles (d = 3.41 nm) was obtained[53]. Korgel et al. utilized a similar approach, with reactions at 1100 °C to 1350 °C respectively, to obtain silicon nanoparticles and then passivated with alkenes by thermal hydrosilylation (Fig.2-7 H), resulting particle sizes between 2.7 ± 0.6nm and 11.8 ± 2.1nm (Fig.2-7 A-G)[29].

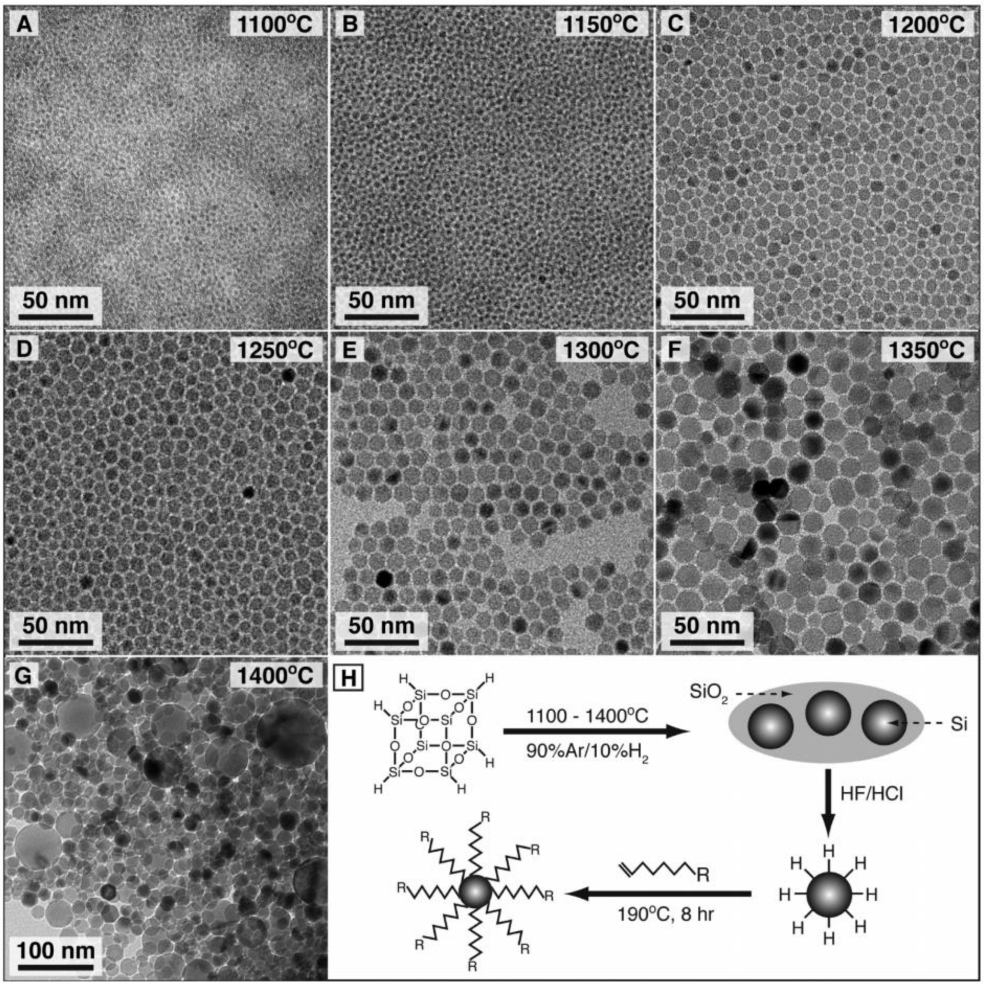


Fig.2-7 (A−G) TEM images of alkene-passivated SiNCs generated at the indicated temperatures; (H) Synthetic pathway of alkyl passivated SiNCs[29]. Adapted with permission from ref. 29. Copyright 2012 American Chemical Society.

In general, this method consists of two steps: thermolysis and etching: thermolysis involves placing HSQ in a reducing gas (5% H_2 and 95% N_2) and keeping it at high temperature for a period of time (1 hour); etching reaction requires etching solution (HF:H_2O:ethanol = 1:1:1) and controlled etching time to achieve the goal.

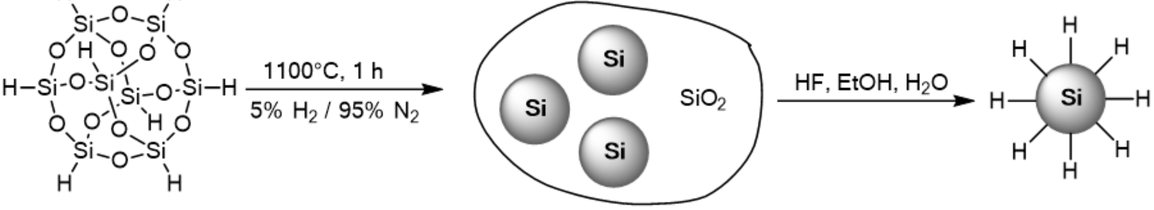


Fig.2-8 Synthesis of SiNCs via thermolysis of hydrogen silsesquioxane.

2.3 Surface Modification of Silicon Nanocrystals

An essential feature of nanoparticles is the huge specific surface area and the large number of volumes to surface ratio. Silicon nanoparticles are no exception. Some estimates suggest that a silicon nanoparticle with a diameter of 2 nm, consisting of 280 silicon atoms and having an orthorhombic dodecahedron, has about 120 atoms (43%) on its surface[54]. It is conceivable that the bonding of surface atoms, i.e., the surface chemistry of silicon nanoparticles, must have a profound impact on the macroscopic properties of the material. The tuning of the optical, electrical and solution properties of the particles by means of ligand exchange aims to extend the many application areas of silicon nanoparticles[55]. Due to the elemental nature of silicon, the modulation of the surface chemistry of silicon nanoparticles is now focused on the formation of more stable silicon-carbon, silicon-nitrogen and silicon-oxygen bonds on the surface of the particles[56].

2.3.1 Hydrosilylation

Hydrosilylation method is one of the most commonly used methods for surface modification of silicon nanoparticles[57]. Bare nuclei with silicon hydrogen bonds on the surface are prepared by electrochemical[58], sintering[59], and low-temperature plasma methods[60], but the silicon hydrogen bonds are highly reactive and easily react with oxygen or moisture in the air, and the nanoparticle surface is oxidized and degraded, and the optical properties are destroyed. By utilizing the reactivity of double and triple bonds of unsaturated olefins or alkynes, the unstable silicon hydrogen bonds are replaced with highly stable silicon carbon bonds through hydrosilylation, and the organic layer can be immobilized to the particle surface to obtain a stable product. It has been shown that the presence of high temperature, UV stimulation and catalysts can initiate[48].

The hydrosilylation reaction is a free radical addition mechanism, and the general pattern is shown in the Fig. 2-9. By heating, the silicon hydrogen bond is cracked to produce the initial free radical, the selection of a high boiling point solvent and olefin ligand is necessary due to the high reaction temperature.

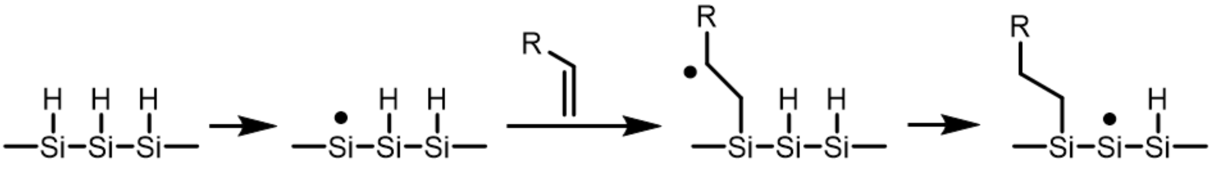


Fig.2-9 Reaction mechanisms for hydrosilylation reaction.

In general, the temperature required for the hydrosilylation reaction of allylbenzene is 160 °C[61], and the hydrosilylation reaction conditions for alkenes are usually 140 °C and 20 hours. It has also been shown that under the conditions of microwave-assisted heating, the process of hydrosilylation reaction can be accelerated and the reaction rate can be increased[62], and the related reaction mechanism is not significantly different from the silicon hydrogenation reaction[63].

Höhlein et al. found that diazonium salts as catalytic systems are capable of introducing aryl groups directly on the surface of silicon nanoparticles by reductive grafting at room temperature[64]. However, the nanoparticles obtained in this way, it has an incomplete organic surface layer and inevitably oxidation reactions. This study also found that diazonium salts can also be used as free radical initiators to initiate silicon hydrosilylation reactions on the surface of silicon nanoparticles, and diazonium salts with electron-absorbing groups have the highest catalytic efficiency, with mild conditions, stable products and short reaction times.

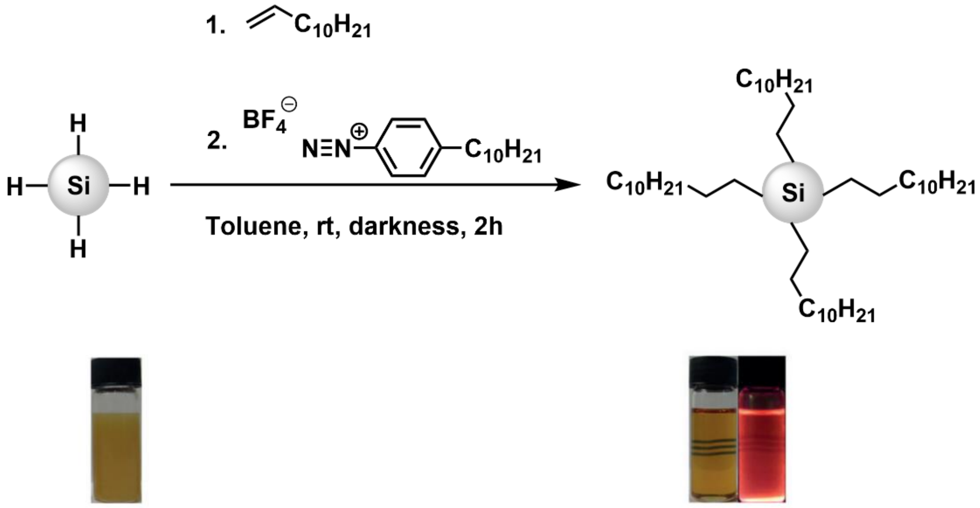


Fig.2-10 Reaction scheme of hydrosilylation reaction initiated by diazonium salts, and unfunctionalized SiNCs in toluene (left), dodecyl functionalized SiNCs in toluene under visible light and UV radiation (right)[64]. Reprinted from ref. 64 with permission.

Purkait et al. discovered that borane can also catalyze silicon hydrosilylation reactions efficiently at room temperature, and that olefins and alkynes with five to twelve carbon atoms can surface coat silicon nanoparticles in the presence of this system[65].

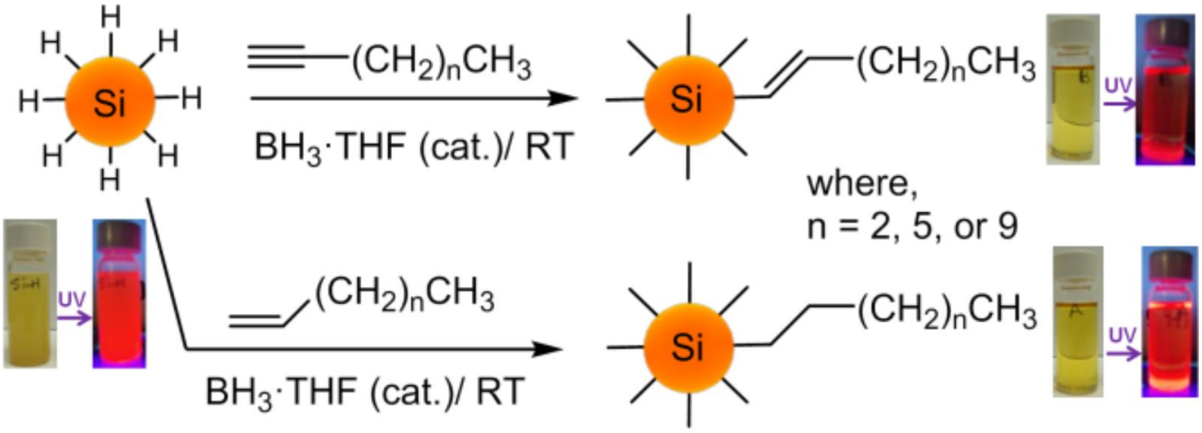


Fig.2-11 Borane catalyzed functionalization of H-SiNCs to yield of alkyl/alkenyl-passivated SiNCs[65]. Adapted with permission from ref. 65. Copyright 2014 American Chemical Society.

The manipulation of the surface of silicon nanoparticles by silicon hydrosilylation addition reactions was the first method to be developed and applied. However, there are still some pressing issues in the field of silicon hydrosilylation reactions, such as the development of simpler and more effective methods for silicon hydrosilylation reaction, the expansion of the variety of molecules for surface modification, and the study of the effects of surface groups on the properties of nucleosomes.

2.3.2 Halogen-ligand Exchange

In order to achieve the modulation of the surface of silicon nanoparticles, it is necessary to synthesize the pristine particles with active chemical bonds (e.g., Si-H, Si-X, X=Cl, Br, I), and subsequently treat them with a series of derivatization reactions to obtain products with different surface properties. Although Si-H bonds are easy to carry out substitution reactions, the grafting efficiency of short-chain gas-phase alkenes/alkynes with lower boiling points tends to be much lower than that of long-chain alkenes/alkynes under existing silicon hydrogenation systems[66]. Nevertheless, the introduction of long carbon chains will form an electrically insulating layer on the surface of silicon nanoparticles, which will impair the optoelectronic properties of silicon nanoparticles and limit its application in optoelectronic devices[67]. The photocatalytic silicon hydrogenation system has high reactivity for short-chain alkenes/alkynes, but for silicon nanoparticles with diameters larger than 5 nm, the homogeneous coverage of surface groups cannot be achieved by photocatalytic methods[68]. Therefore, the development of new surface modification methods deserves attention. Si-X (X=Cl, Br, I) bonds, which have greater polarity than Si-H bonds, graft short-chain alkenes-alkynes on the surface of silicon nanoparticles via a haloalkylation reaction pathway, which has been demonstrated in bulk silicon materials[69], and the research on the reactivity of silicon-halogen bonds on the surface of silicon nanoparticles is continuing.

In general, nanoparticles with Si-X (X=Cl, Br, I) bonds on the surface can be obtained after the reduction of silicon halide using Zintl salts in reaction with $SiCl_4/Br_2$ or by using a strong reducing agent[39]. Strong nucleophilic reagents with negative electron groups (e.g., RLi, RMgX, X=Cl, Br, I) can directly react with the Si-X (X=Cl, Br, I) bonds in a halogenated manner, introducing aliphatic or aromatic hydrocarbon groups to the surface of the silicon nanoparticles[38]. Unfortunately, the products obtained by this method are usually poorly dispersed, the emission wavelengths are mainly in the blue wavelength range, and it is difficult to obtain a large number of products in a macroscopic sense.

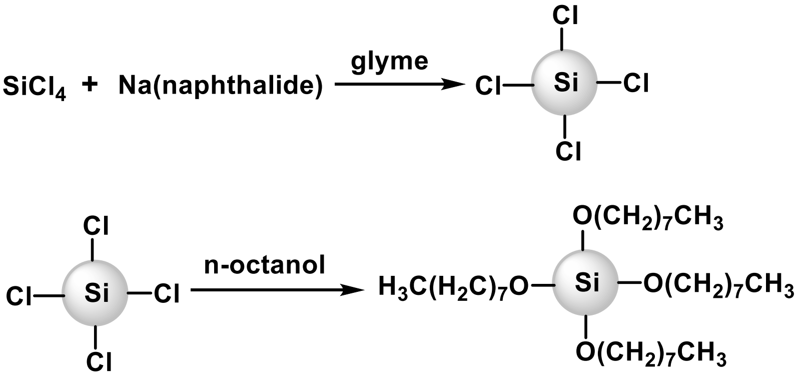


Fig.2-12 Reduction with sodium naphthalide followed by termination.

In response to these problems, Dasog et al. prepared homogeneous particle size, H-terminated silicon nanoparticles by sintering and subsequently treated their surfaces with halogen monomers and compounds (e.g., Br_2, I_2, PCl_5) to obtain products with surfaces covered by Si-X (X=Cl, Br, I) bonds[70]. The halogenated products were further investigated by alkylation substitution reactions of Grignard's reagent with Si-X (X=Cl, Br, I) bonds, and the products obtained by Si-Cl and Si-Br bonding reactions were shown to be more stable and those obtained by Si-I bonding to be comparative less stable. The implications of this research are that it develops new ideas for alkylation modifications on the surface of silicon nanoparticles. The group also achieved the preparation of silicon nanoparticles that emit light in the full visible spectrum by combining variety of treatment with a single tuned surface ligand[71] (Fig.2-13).

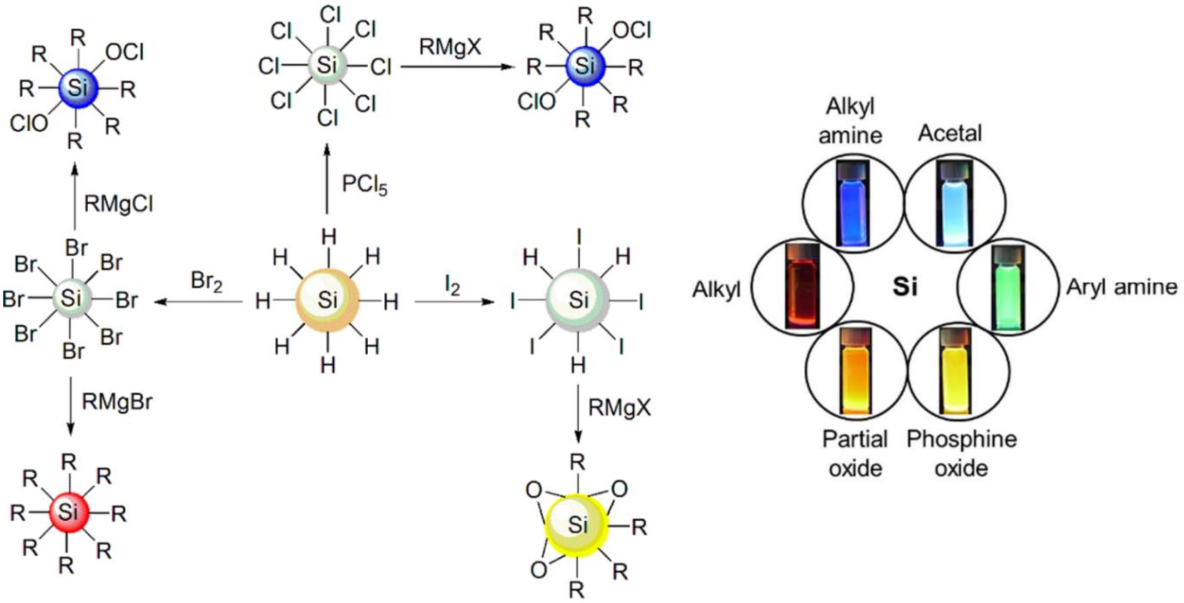


Fig.2-13 (Left) Halogenation and alkylation of hydride terminated SiNCs[70] Adapted with permission from ref. 70. Copyright 2015 American Chemical Society; (Right) SiNCs under UV light[71]. Adapted with permission from ref. 71. Copyright 2014 American Chemical Society.

Other researchers have found that surface treatment of Si-Cl bonded silicon nanoparticles with methanol/water yields $-OCH_3$ modified products, the methoxy subsequently hydrolyzed to hydroxyl groups and reacted with alkyltrichlorosilane reagents to ultimately yield siloxane-coated silicon nanoparticles[72] (Fig.2-14). The reaction of the allylamine/reducing agent $LiAlH_4$ and the Si-Cl bond gives a product with a Si-NH-butyl surface group[73].

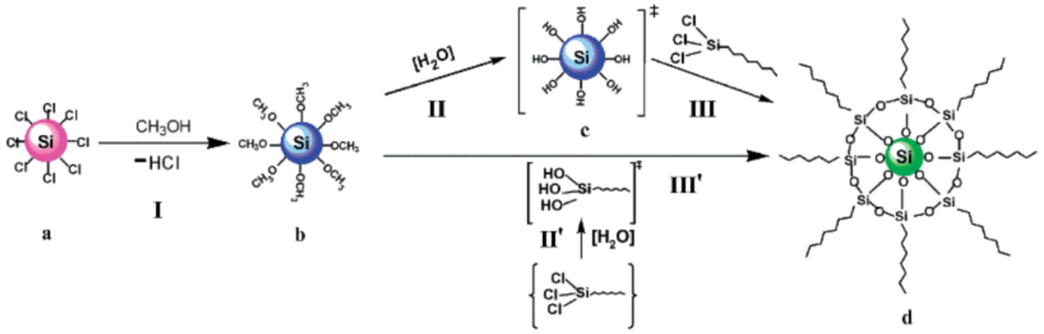


Fig.2-14 Three-step termination route with the proposed silanization process[72]. Adapted with permission from ref. 72. Copyright 2004 American Chemical Society.

The halogenation reaction requires a lower temperature compared to the silicon hydrogenation reaction and effectively increased the grafting efficiency of short chain alkanes. On the downside, the doping of halogen elements had a significant effect on the fluorescence properties of the silicon nanoparticles, and the effect varied from halogen to halogen. In conclusion, the surface modification of nanoparticles covered with Si-X bonds shows new potential, but the preparation methods and mechanisms still need further research.

2.3.3 Organolithium Reagents Functionalization

Over the past years, researchers have conducted in-depth studies on the luminescence mechanism of silicon nanoparticles[74]. The photoluminescence mechanism of silicon nanoparticles has not been fully explained due to the fluorescence complexation mechanism, surface defects and excitation mechanism of ligands[75]. When the size of the silicon material is reduced to the Bohr radius, the chance of electron and hole complexation is enhanced and fluorescence can be generated by relaxation. In addition, the surface of hydrogen, oxygen or halogen capping occurs during the preparation of silicon nanoparticles, which do not have a semiconductor barrier layer matching the crystalline form, so the surface effect affects the photoluminescence performance, including fluorescence quantum yield, fluorescence emission peak position and fluorescence lifetime[76].

In previous work in our group, organolithium reagents were employed to modify H-terminated silicon nanoparticles. The reaction temperature was room temperature conditions and the reaction time was short. A plausible reaction mechanism is shown in Fig. 2-15, where the Si-Si bond is cleaved, the Si-C bond is formed and the highly reactive Si-Li bond is quenched by protons or deuterons[77].

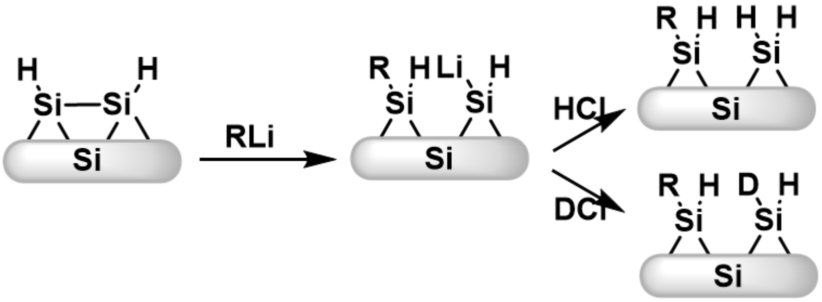


Fig.2-15 Reactivity of organolithium reagents towards nanostructured silicon surfaces.

By employing an organolithium reagent to modify the silicon nanoparticles, the phenylethynyl group is grafted onto the surface to give a Si-C≡C- bonding product. It is novel that the photoluminescence spectrum exhibits a peak redshift. Combining scanning tunneling spectroscopy (STS) measurement, the photoluminescence of phenylethynyl functionalized SiNCs redshift can be explained by the following mechanism: the transition across in-gap state reduces the apparent band gap of the recombination process[78].

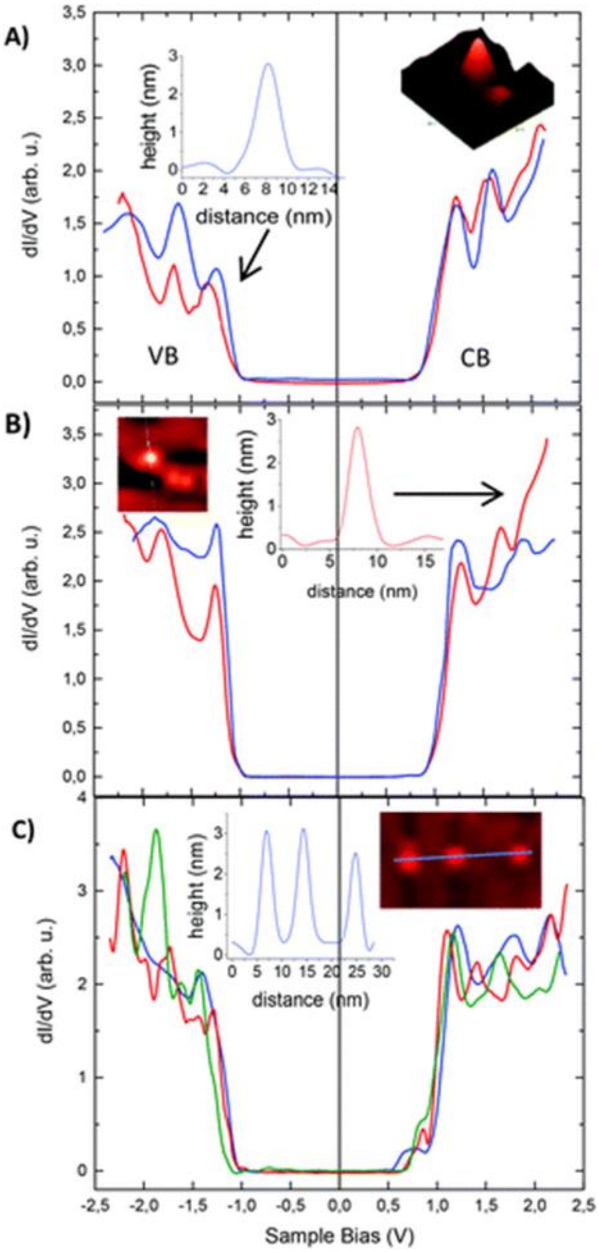


Fig.2-16 Tunneling spectra measured on ~3 nm SiNCs functionalized with (A) n-hexyllithium; (B) phenyllithium; (C) lithium phenylacetylide[78]. Adopted from ref. 78 with permission from The Royal Society of Chemistry.

Based on the large specific surface area and Si-Si defects, silicon nanoparticles have a much higher surface activity compared to conventional bulk materials, so it is necessary to improve their luminescence properties through surface modification. By modifying silicon nanoparticles, it is possible not only to modulate the particle size but also to change the surface chemistry and enrich the field of application[79]. Over the past decades of research, various methods and ligands have been generated to modify silicon nanoparticles, but in many fields, it is still unsatisfying and more exploration is required.

2.4 Applications of Silicon Nanocrystals

Silicon is an indirect bandgap semiconductor with poor photoluminescence properties when present in bulk form, however, when the size is reduced to the nanoscale, the quantum-limited effect of silicon nanoparticles comes into play significantly and potential applications have been extended to LED optoelectronic device, sensor, solar cells and biomarkers[80].

2.4.1 LED Optoelectronic Device

White LEDs have the advantages of long lifetime, high efficiency and low energy consumption[81]. Since the photoluminescent properties of silicon nanomaterials have been proven, related research on silicon-based nanomaterials in the field of white LEDs has been continuously explored[82]. Yang et al. have treated small fluorescent silicon nanoparticles (~3.7nm) as a class of color converters for blue LED chips to resulting white LEDs and successfully synthesized tunable fluorescent silicon nanoparticles ranging from blue to yellow-green (Fig. 2-17 a and c)[83]. The silicon nanoparticles with an emission spectral range of yellow-green form the basis of the white spectrum when the pH is 4 and so are utilized as a color converter for the construction of white LEDs. The final resulting LED devices show a luminous efficiency of 131 mW^{-1}, with an International Commission on Illumination chromaticity coordinate of (0.3041, 0.3129), a color rendering index of 82 and an associated color temperature of 7982K (Fig. 2-17 e).

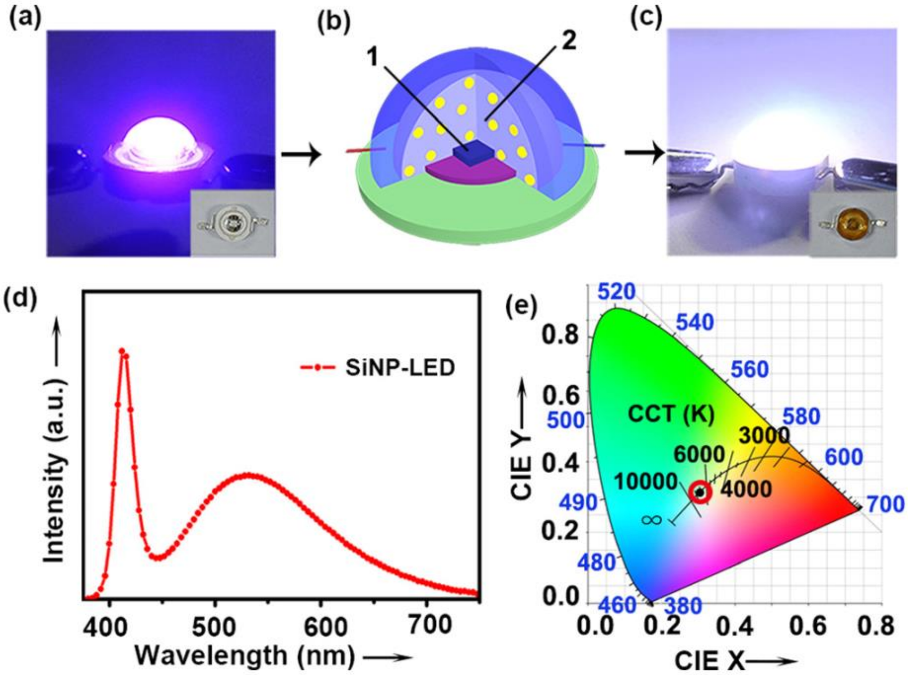


Fig.2-17 (a) Photographs of the blue LED. (b and c) SiNCs-based white LED. (d) Spectra of SiNCs-LED. (e) The color spectrum on the CIE color space[83]. Reprinted from ref. 83 with permission.

Mock et al. modified silicon nanoparticles utilizing three alkyl ligands and applied them to LEDs to study the optoelectronic properties (Fig. 2-18). The use of organolithium reagents allowed the surface coverage to be reduced to just under 50%, while maintaining colloidal stability. Improved properties of silicon nanoparticle LEDs can be achieved by modulating long and short surface ligands[84].

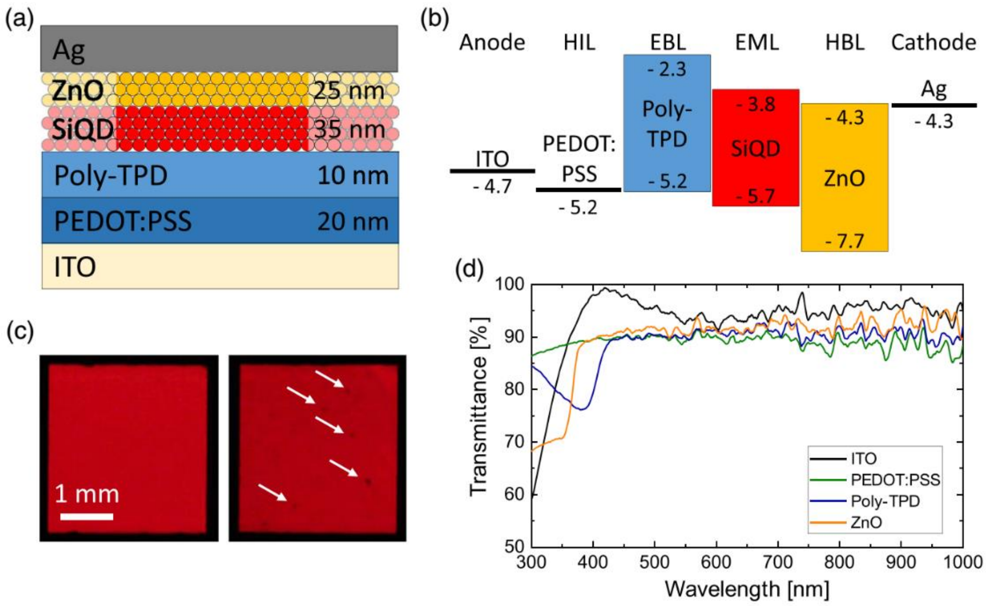


Fig.2-18 a) Schematically SiNC-LED stack. b) Proposed energy diagram. c) Microscope images of the EL of SiNC-Hex LEDs. d) Transmission spectra[84]. Reprinted from ref. 84 with permission.

Researchers develop a stable Si-based light-emitting diode by modifying silicon nanoparticles with microencapsulation and specific ligands[85]. Additional investigations have shown that changing the annealing temperature and the ratio of SiNCs to HSQ in the active layer can improve the performance of LEDs[86].

2.4.2 Sensor

The superior fluorescence properties[87], high fluorescence intensity and good photostability of silicon nanomaterials make it possible to establish stable and sensitive detection methods[88]. In recent years, there have been an increasing number of reports on the use of nanoparticles in analytical assays[35, 89]. Water-soluble functional groups can be designed to modify the surface of nanomaterials to improve their water solubility and to react with organic molecules or metal ions, resulting in changes in fluorescence, and are therefore employed for the analytical detection of organic molecules or metal ions.

Water-soluble silicon nanoparticles are generally encapsulated by amino or carboxyl groups. To prepare water-soluble silicon nanoparticles, Meng et al. used a hydrothermal method to obtain -NH_2-covered SiNCs and detected manganese ions as a fluorescent probe in the linear range of 2.5 ~ 250 μM with a detection limit of 1.1 μM[34]. Zhang et al. demonstrated that dopamine is the only organic molecule that can quench its fluorescence, so this burst effect can be detected by using the microwave method[90]. The mechanism of the dopamine assay is given in Fig. 2-19.

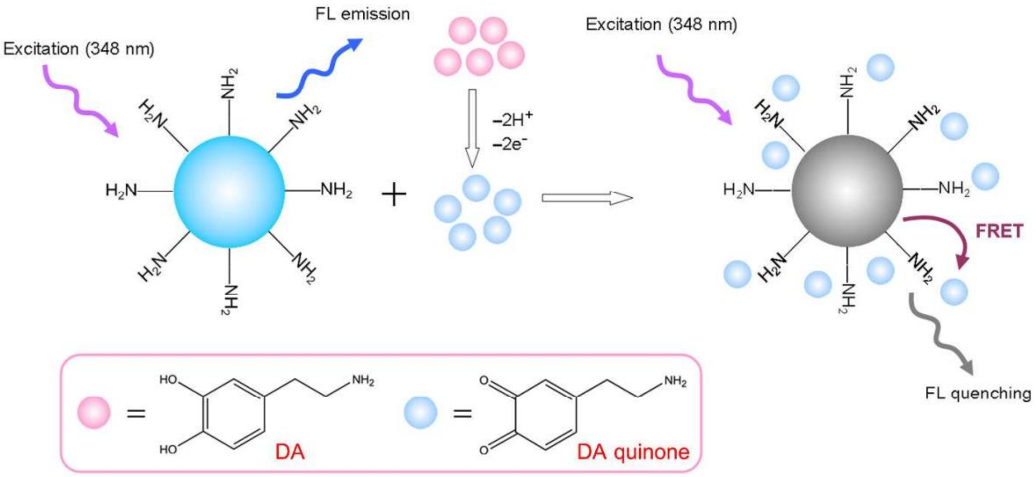


Fig.2-19 Mechanism of the dopamine detection using SiNCs[90]. Adapted with permission from ref. 90. Copyright 2015 American Chemical Society.

In addition, fluorescent SiNCs have been used for in vivo/in vitro pH detection. In 2016, Chu et al. synthesized pH sensors using surface functionalization of silicon nanoparticles with pH-sensitive dopamine molecules and insensitive rhodamine B isothiocyanate (RBITC) molecules, for the first time, real-time and prolonged pH collection in cells has been achieved[91]. The SiNCs prepared as described above exhibit a wide pH response (pH=4-10), strong fluorescence (quantum yields of 15-25%), excellent photostability (loss of fluorescence intensity of approximately 9% after 40 minutes of continuous UV irradiation) and low toxicity (cell viability of over 95% during the 24-hour treatment period).

In addition to these applications, SiNCs-based fluorescent sensors have also been used to detect DNA. By measuring the change in fluorescence intensity due to the change in multicolor molecular beacon (MBS) conformation caused by DNA hybridization, the SiNCs fluorescence sensor modified with gold nanoparticles can easily detect the DNA to be measured[92]. More importantly, compared to free nanogold, which is relatively less salt stable (e.g., high salt concentrations lead to significant aggregation of nanogold), nanogold-modified fluorescent silicon nano sensors are resistant to high temperatures and salts. MBS sensors based on nanogold-modified fluorescent SiNCs can detect multiple DNA targets simultaneously, due to the ability of different DNA strands to assemble in such multicolor beacons. DNA strands can be assembled on the large surface of this MBS sensor[93].

2.4.3 Solar Cells and Energy Storage

With the emergence of some non-renewable resources such as oil and coal, whose overuse has had an extremely degrading effect on the environment, clean and renewable energy sources that are not harmful to the environment are undoubtedly the major challenge facing mankind today. The most effective way to solve these problems is through the use of solar energy. Solar energy is not only an environmentally friendly and renewable resource, it is also an inexhaustible source of new energy. Many researchers are now working on solar cells, making a significant contribution to the development of new applications for solar energy resources. Although the high production costs and low conversion efficiency of solar cells have been criticized to date, their advantageous properties and the scarcity of energy from coal, oil and natural gas have forced people to look for high conversion efficiency and low-cost solar cell materials. At present, organic solar cells, monocrystalline silicon solar cells, and dye-sensitized solar cells have received the most attention from researchers. Obtaining low-cost, high-efficiency solar cell materials is the key to utilize solar energy effectively.

Quantum dot solar cells are one of the most sophisticated solar cells available, as they can increase photovoltaic conversion efficiency to approximately 66% theoretically by creating higher photovoltage and photocurrent through photogenerated carriers. Compared to conventional solar cells, this photovoltaic conversion efficiency is worthwhile. The range of advantages offered by silicon nanomaterials provides the basis for their application in the field of quantum dot solar cells. Using magnetron sputtering, Cho et al. prepared phosphorus-doped silicon nanoparticles by alternating the deposition of SiO_2 and SiO_x using Si, SiO_2 and P_2O_5 as targets, and then deposited the phosphorus-doped silicon nanoparticles on a silicon substrate using silica as a substrate[94]. The highest conversion efficiency of 10.6% was obtained by varying the parameters such as the particle size of the silicon nanoparticles and the thickness of the silicon dioxide substrate, the structure of which is shown in Fig.2-20.

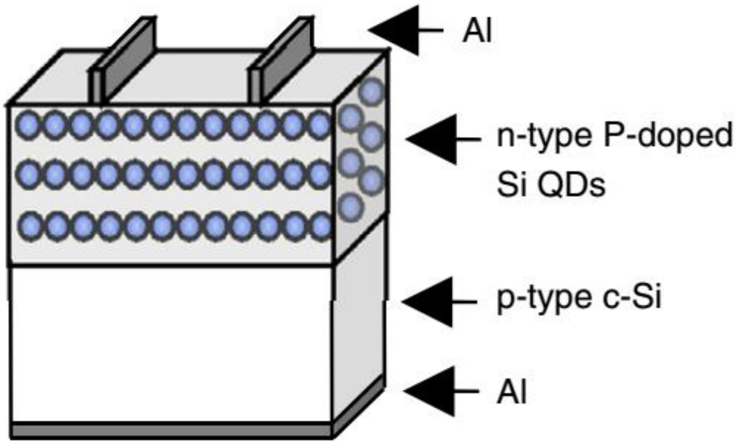


Fig.2-20 Structure of the SiNCs solar cell[94]. Reprinted from ref. 94 with permission.

Solar energy is a renewable source of energy and solar cells convert solar energy into electricity via photovoltaic effect[95]. SiNCs can be easily dispersed on lightweight conductive graphene. On the one hand, graphene paper made from stacks of graphene sheets is electrically conductive, has high mechanical strength and has a storage volume comparable to that of lithium[96]. On the other hand, graphene is cheap to prepare, simple and easily scalable, and its application in the preparation of batteries can be a powerful support for other high storage capacity materials. Graphene-supported silicon nanomaterials have been successfully developed to produce composite anode materials for lithium batteries (e.g., Fig.2-21), with high energy storage volumes in the graphene-silicon nanomaterials composite[97]. Commercially available silicon nanoparticles, PEDOT:PSS and formic acid, were added to the mortar and fully ground to obtain the desired electrode material (Fig. 2-21). Due to the presence of silicon nanomaterials and graphene materials, the loss of battery capacity can be effectively reduced during the lithiation and de-lithiation process.

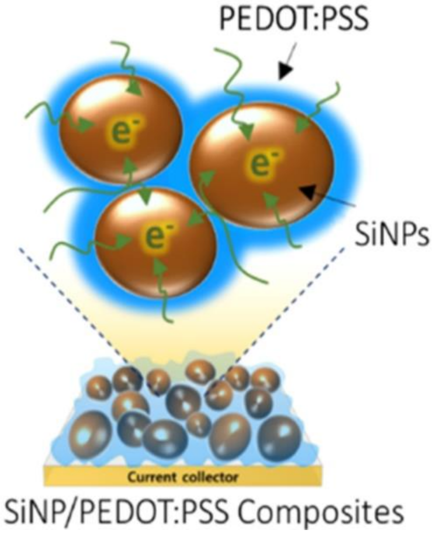


Fig.2-21 Scheme for the PEDOT:PSS/SiNCs electrode[97]. Adapted with permission from ref. 97. Copyright 2016 American Chemical Society.

2.4.4 Biomarkers

Fluorescent cell probes are very useful for studying the morphology, activity and physiological role of cells. To facilitate the observation and tracking of biological cells, these probes must be water dispersible, bleach resistant, fluorescent luminescent properties[98] and biocompatible[99]. Silicon nanomaterials have all these strengths, which makes it possible to apply them in the field of biofluorescent labelling. The quantum-limited effect of silicon nanoparticles is a research direction of particular interest as it may enhance the possibility of luminescence complexation through an indirect versus direct band gap transition that would enhance the fluorescence intensity of silicon nanoparticles[100]. Although the excited luminescence of silicon nanoparticles is weak, their biocompatibility and cellular non-toxicity offer significant advantages over conventional group II/VI quantum dots[101]. And because of their biocompatibility, silicon-containing materials have applications in cell imaging and cell labelling. But only if the prepared silicon nanoparticles are stable and fluorescent and have good water dispersion.

Silicon nanomaterials are not only non-toxic but also biocompatible, and more suitable than other nanomaterials for biomarkers[102]. Park et al. produced nanoporous silicon using electrochemical etching and used it for the first time for fluorescent labelling of living biological tumors[21a]. They injected nanoporous silicon as a drug carrier into mice and monitored the photoluminescence of nanoporous silicon, thereby determining the accumulation and degradation in the mice. Ultimately, it was observed that nanoporous silicon accumulated mainly in organs associated with the monocyte-macrophage system (MPS) and degraded to apparently non-toxic products within a few days, which were excreted from the body via the urinary system.

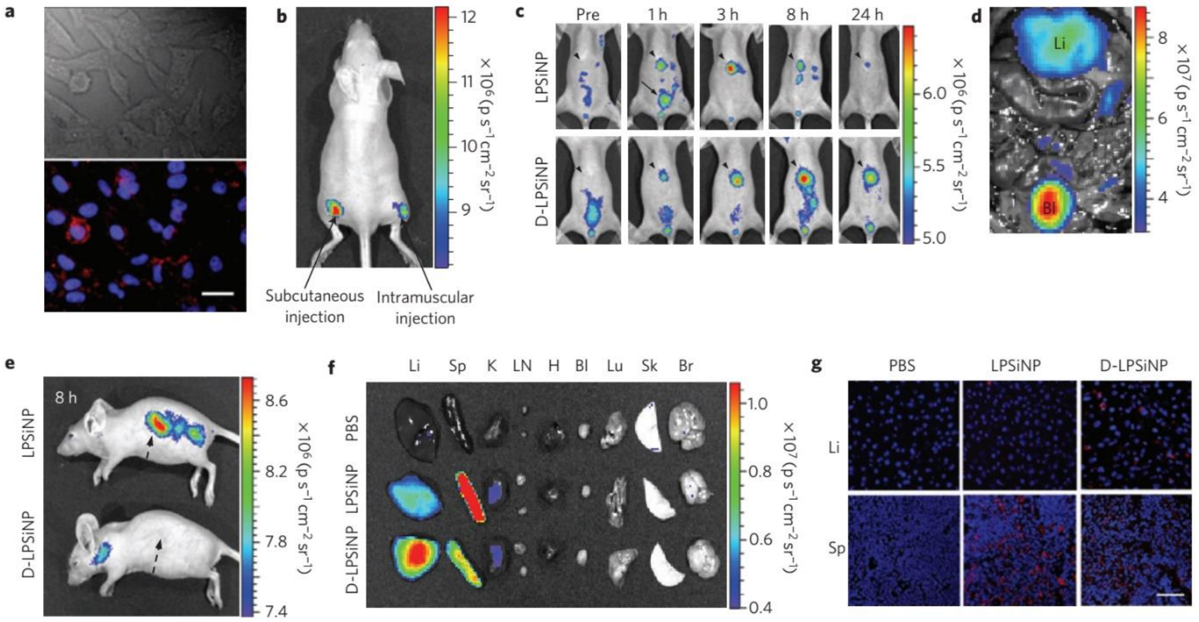


Fig.2-22 In vitro, in vivo and ex vivo fluorescence imaging with LPSiNCs[21a]. Reprinted from ref. 21a with permission.

Over the years, researchers have explored various fields of silicon nanoparticles applications, also including potential applications such as drug delivery. Grötsch et al. have discovered a novel dissipative self-assembly of photoluminescent silicon nanoparticles, a process driven by chemical fuels (Fig.2-23)[103]. 5-hexenoic acid modified silicon nanoparticles were used as precursors and the nanoparticles became water soluble after surface functionalization. 2-(N-morpholino) ethanesulfonic acid (MES) with N-hydroxysuccinimide (NHS) in water were applied as the buffer solutions. The carboxylate groups, which were grafted on the silicon nanoarticles surface in the starting step, combine with 1-Ethyl-3-(3- dimethylaminopropyl) carbodiimide (EDC) to form NHS-esters, and the process is irreversible. EDC is consumptive; thus, the addition of EDC is regulated to control the process.

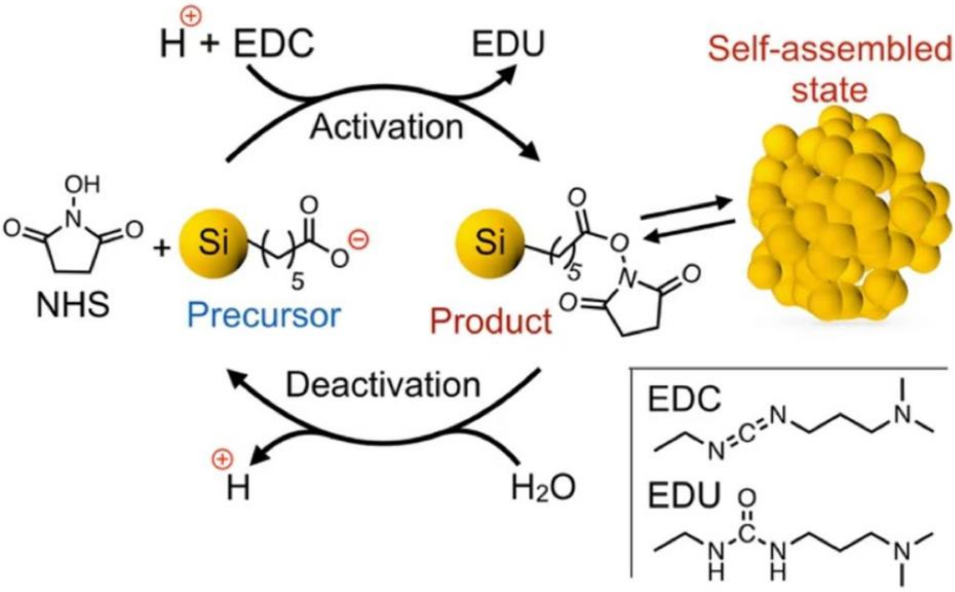
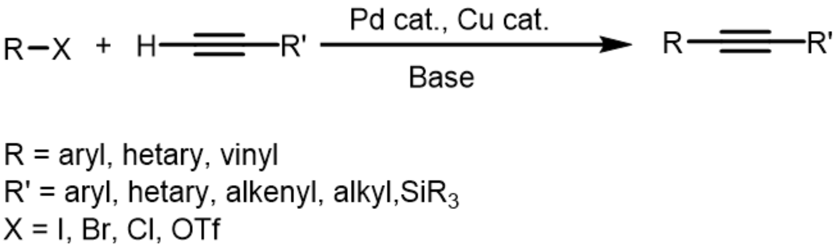


Fig.2-23 Schematic of the chemical reaction network[103]. Reprinted from ref. 103 with permission.

2.5 Synthesis Routes for Ethynylaryls

One of the most fundamental and typical reactions in organic chemistry is the formation of C-C bonds. In most of these reactions, transition metals are commonly used as catalysts, and among them, palladium-based catalysts have had the widest range of applications in C-C bond formation in recent years[104]. Catalytic C-C bond formation by palladium-based catalysts in the Sonogashira[105] and Heck[106] reaction is considered to be an excellent tool for various organic transformations in academic and industrial processes. During the decades-long exploration and research, though, a large number of exciting results have emerged[107].

In 1975 the reaction was first reported independently by Sonogashira[108], Heck[109] and Cassar[110]. The original Sonogashira reaction was a reaction in which aryl halides were coupled with terminal acetylene in the presence of a palladium catalyst, a copper co-catalyst, and an amine as a solvent or a base. However, it is not in line with the concept of green chemistry because copper salts are harmful to the environment and difficult to recover. In addition, if the copper acetylenes are exposed to air or in contact with oxidizing agents, in addition to the target product, this leads to a side reaction that produces the terminal acetylenes' own coupling product, the Glaser reaction, which reduces the utilization of the raw material and makes the isolation and purification of the target product difficult.



R = aryl, hetary, vinyl
R' = aryl, hetary, alkenyl, alkyl,SiR_3
X = I, Br, Cl, OTf

Fig.2-24 The general scheme of Sonogashira reaction.

Since 1975, the mechanism of Sonogashira reaction has been studied without interruption, but without copper participation, it has been mostly inferred based on experimental results and still has not been confirmed by consensus. At present, the widely accepted mechanism is as follows: in the first step, the aryl halide undergoes oxidative addition to form the $Pd(0)L_n$ complex, i.e., Intermediate 1 ($RPdXL_2$); in the second step, a substitution reaction with $RPdXL_2$ using alkynes as ligands to produce Intermediate 2, i.e., $RPdL_2CH{\equiv}CR'$; in the third step, Intermediate 2 is deprotonated to give Intermediate 3, i.e. $RPdL_2C{\equiv}CR'$, which is reduced by elimination to give the coupling product $RC{\equiv}CR'$ and produce the active substance $Pd(0)L_n$ to continue into the cycle reaction.

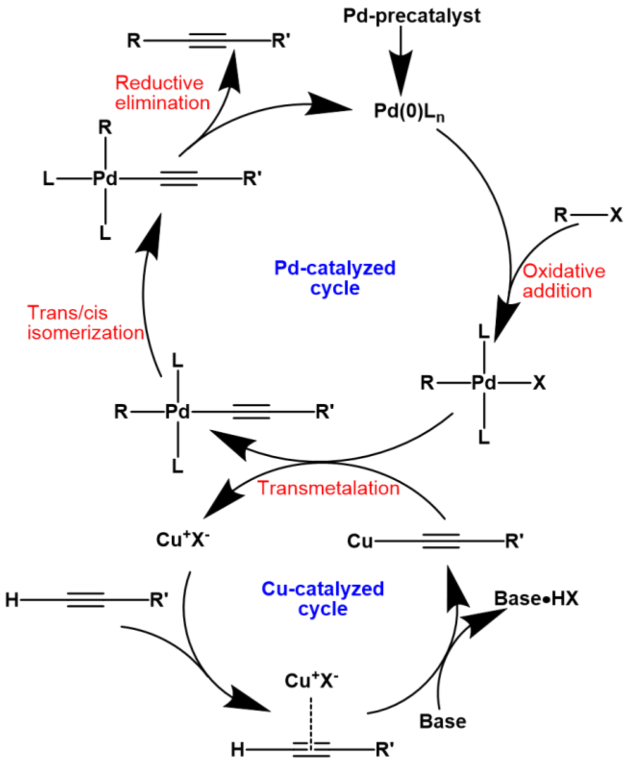


Fig.2-25 Schematic spectrum of Sonogashira reaction mechanism[111].

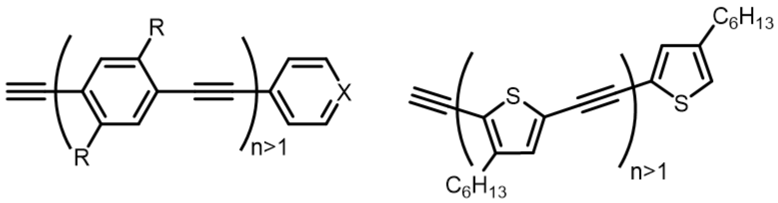
Homogeneous catalysts can be directly dissolved in solution, so most of them have extremely efficient catalytic effects, but they also make the catalysts not easy to be separated from the solution. With the gradual emphasis on environmental friendliness and economic cost, loaded catalysts, which have the advantages of mild reaction conditions, easy operation, easy purification and separation, and multiple recycling of catalysts, are receiving more and more attention. In recent years, a large number of studies have reported examples of using different materials as catalyst carriers, such as the use of carbon materials such as activated carbon, CNT, graphene; polymer materials such as polyaniline, PVP, hydrogel and metal materials such as ferric oxide and alumina[112].

3 Motivation of Project and Research Content

From the above review, it is clear that SiNCs have unique optical/electrical properties, excellent resistance to photobleaching, positive water solubility, easy surface functionalisation, good biocompatibility and low toxicity, and the research on SiNCs in the field of optoelectronic devices and fluorescent nanomaterials is being expanded, which is the basis for the wide application of SiNCs. The synthesis of SiNCs and some of their luminescence mechanisms have been gradually improved, but the prepared SiNCs are not stable, the surface ligands are not sufficiently developed, the fluorescence is single-emission and the emission wavelength is in the short-wave region.

Surface functionalization of SiNCs with conjugated π-systems could be promising for applications in electronic devices, because they might offer the possibility of charge transfer from/to the SiNCs or give rise to unforeseen properties. Besides, these surface groups can offer favorable interface to conjugated polymers to form hybrid composites with improved properties.

The aim of the project is to design conjugated systems with alkynyl end groups and attach them to SiNCs surfaces. Alkynyl end groups are required for the subsequent SiNCs surface functionalization reactions. Following systems with exact control on repeating units are suggested in Fig. 3-1 and the organic synthesis mechanism can be found in the previous chapter (chapter 2.5).



R=H, $-C_6H_{13}$
X=C, N

Fig.3-1 Alkynyl end groups.

Organolithium reagents functionalized SiNCs have been investigated by many groups. This method allows the direct grafting of alkynyl end groups onto the surface of SiNCs without disrupting the carbon-carbon triple bond, and the photoluminescence of the modified SiNCs is red-shifted. For this project, the obtained alkynyl end groups can be subsequently synthesized as organometallic reagents, which can later be applied to modify the hydrogen-capped SiNCs. In addition, dodecene-modified silicon nanoparticles will be obtained by hydrosilylation and used as a standard comparison.

Surface functionalization can be achieved via organolithium reagents or hydrosilylation as shown in Fig. 3-2.

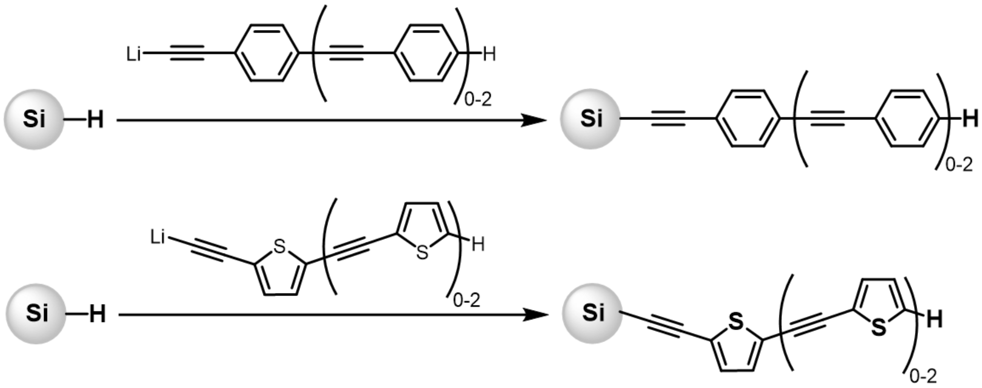


Fig.3-2 Surface functionalization.

Upon successful surface functionalization, SiNCs would be characterized in detail (FTIR, PL, TGA) and their application in optoelectronic devices prototyped. The results are expected to demonstrate the following issues: 1) whether there is a significant change in FTIR; 2) whether photoluminescence is still present and can produce redshift; and 3 whether there is an increase in the surface coverage of SiNCs.

Alkynyl end groups modified silicon nanoparticles have also been endowed with certain potential applications, including, but not limited to, enhancing the conductivity of conducting polymers (PEDOT:PSS).

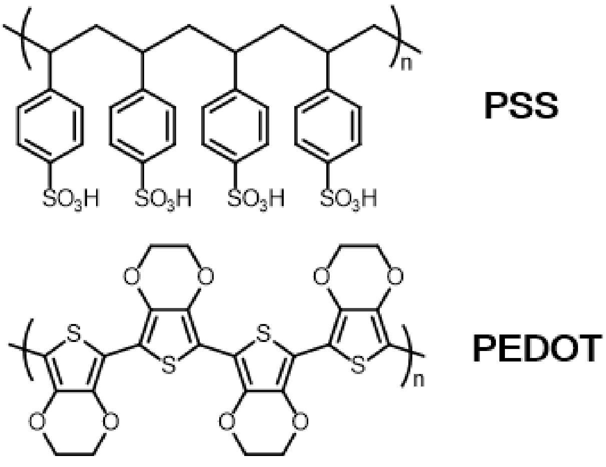


Fig.3-3 Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS).

4. Synthesis of Alkynyl End Conjugated Groups and Surface Functionalization of SiNCs

4.1 Design and Synthesis of Conjugated Surface Systems with Alkynyl End Conjugated Groups

4.1.1 Design of Alkynyl End Conjugated Groups

Polyarylacetylene is a class of rigid conjugated polymers containing $C\equiv C$ in the main chain, with good thermal stability, electroluminescence, so it has a wide range of applications in the fields of electroluminescent devices, sensors and so on[113]. In order to explore the properties of the alkynyl end aryl groups and to expand its applications, they were modified onto the SiNCs surface.

The Sonogashira coupling reaction is well known to generate conjugative enynes and arylalkynes. In the reaction, Pd species are used as a catalyst, Cu is used as a cocatalyst, and aryl or vinyl halides are used as starting material with terminal alkynes. The reaction occurs in the presence of a polar solvent and an amine base.

Alkynyl end groups are required for the subsequent SiNCs surface functionalization reactions. The surface moieties were designed from simple to multiple. The following systems with exact control on repeating units are suggested:

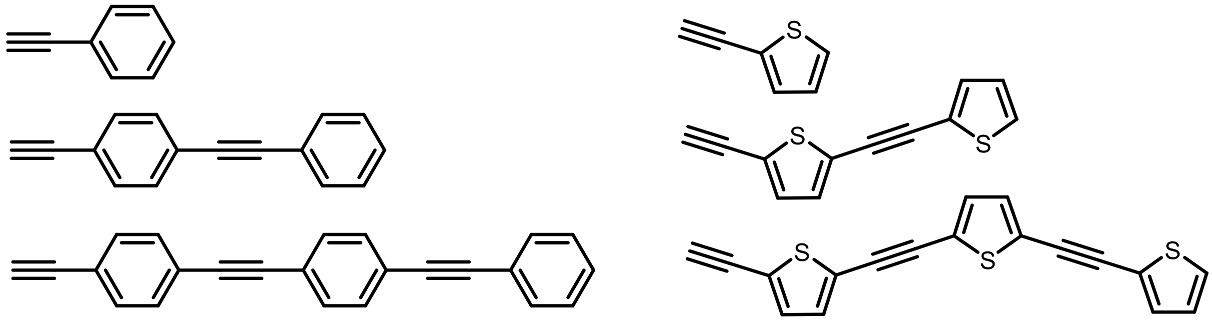


Fig.4-1 Different conjugative surface groups

Synthetic route of two different species conjugative systems

The designed conjugated systems can be obtained very precisely based on the Sonogashira coupling reaction and deprotection reaction.

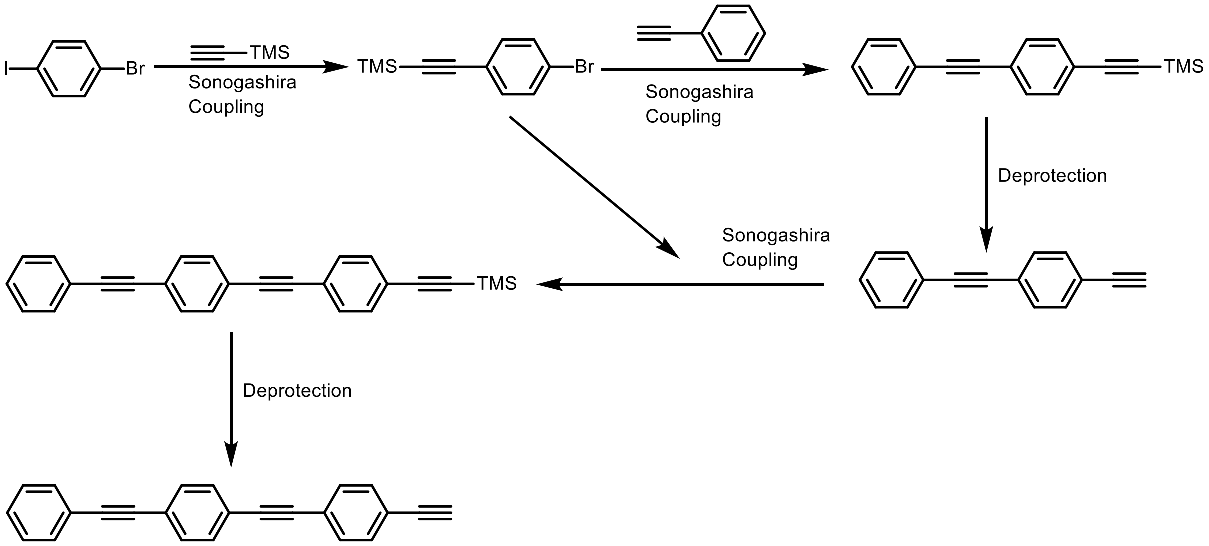


Fig.4-2 Synthetic route of phenylacetylene conjugative systems

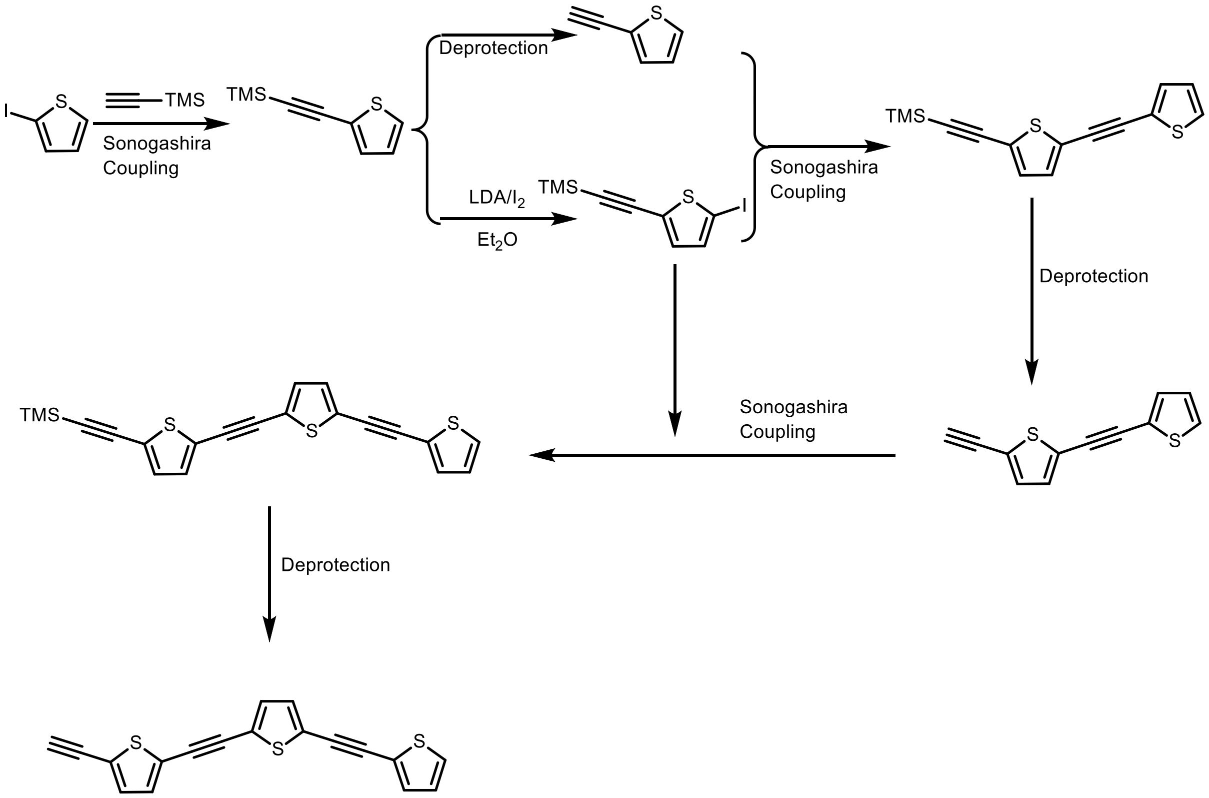


Fig.4-3 Synthetic route of ethynylthiophene conjugative systems

4.1.2 Results and Discussion of Synthesized Alkynyl End Conjugated Groups

Organic conjugated groups were synthesized by Sonogashira coupling reaction and deprotection reaction. After purification, A range of characterisation tools were used to detect the presence and properties of surface groups, including ^{1}H-NMR, ^{13}C-NMR, FTIR, PL and UV-Vis.

^{1}H-NMR spectroscopy provides a great deal of valuable information for the structural analysis of organic compounds through the chemical shifts, coupled splitting and integration of the relevant hydrogens. Conventional hydrogens, such as alkyne and aromatic hydrogens, are well characterised in the hydrogen spectra and can be easily attributed. The horizontal coordinate of a ^{13}C-NMR spectroscopy is the chemical shift and the vertical coordinate is the intensity of the peaks, the height of which approximates the number of carbon atoms. All NMR spectroscopy are presented in the experimental section (chapter 7.2).

Fourier Transform Infrared Spectra (FTIR)

FTIR spectra mainly provides a wealth of structural information about the functional groups and chemical bonds of molecules. Usually organic molecules for multi-atomic combination of complex molecules, a variety of chemical bonds and groups of vibration spectral addition and spatial configuration of the influence of the combined frequency, differential frequency, resonance, rotation and other spectral microstructure of many peaks of the combination of complex spectra. However, combining the previous reaction design, ^{1}H-NMR and ^{13}C-NMR spectroscopy, accurate results can be obtained.

In the FTIR spectra (Fig. 4-4) of phenylacetylene conjugative systems, alkynyl C-H bonds and aryl C-H bonds can be founded at 3295 – 3260 cm^{-1} and 3084 – 3050 cm^{-1} respectively. The weak bands (2112 cm^{-1}) imply the existence of C≡C of conjugative systems. Clear evidence of aromatic C=C bending is confirmed at 1601 – 1442 cm^{-1} which is considered as a typical symbol of the phenyl group.

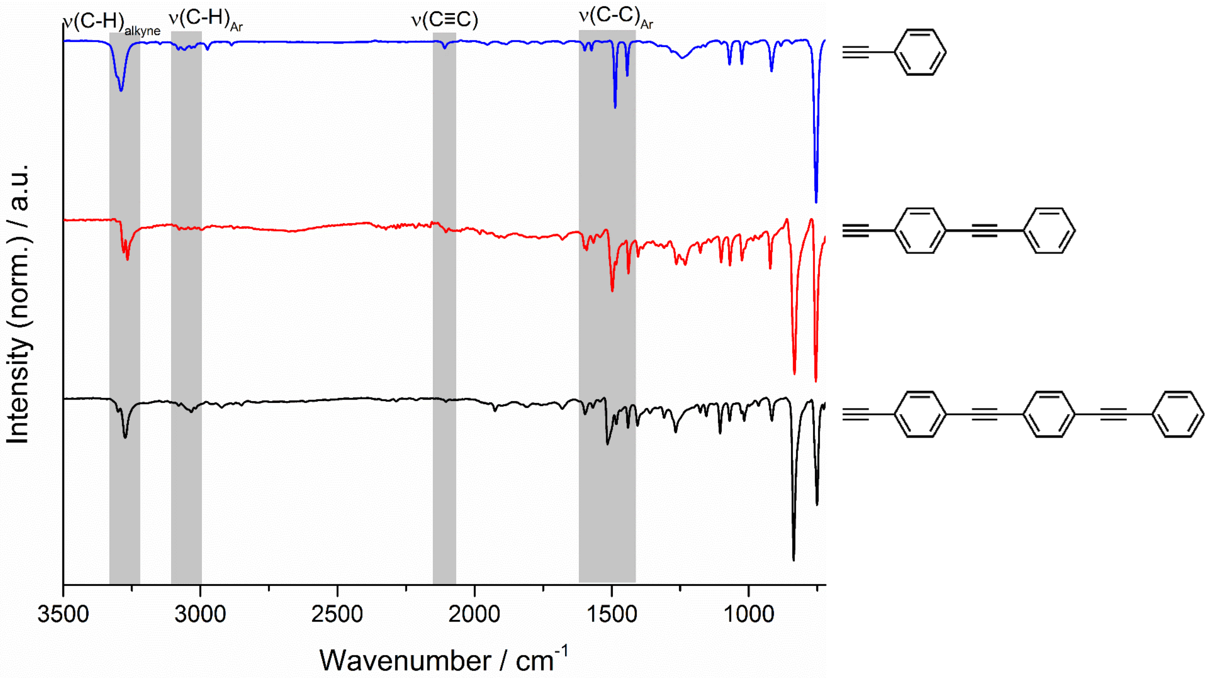


Fig.4-4 FTIR spectra of phenylacetylene conjugative systems: PE-1 (blue), PE-2 (red), PE-3 (black)

In the FTIR spectra (Fig. 4-5) of ethynylthiophene conjugative systems, strong sharp alkynyl C-H stretch is observed at 3294 cm^{-1}. Meanwhile aryl C-H stretch can be founded at 3084 – 3050 cm^{-1}. ET-1 shows alkynyl C≡C stretch at 2105 cm^{-1}. ET-2 and ET-3 show two different alkynyl C≡C stretch at 2198 cm^{-1}and 2101 cm^{-1}. Obviously, 1540 – 1421 cm^{-1} is the evidence of aromatic C-C ring-stretching.

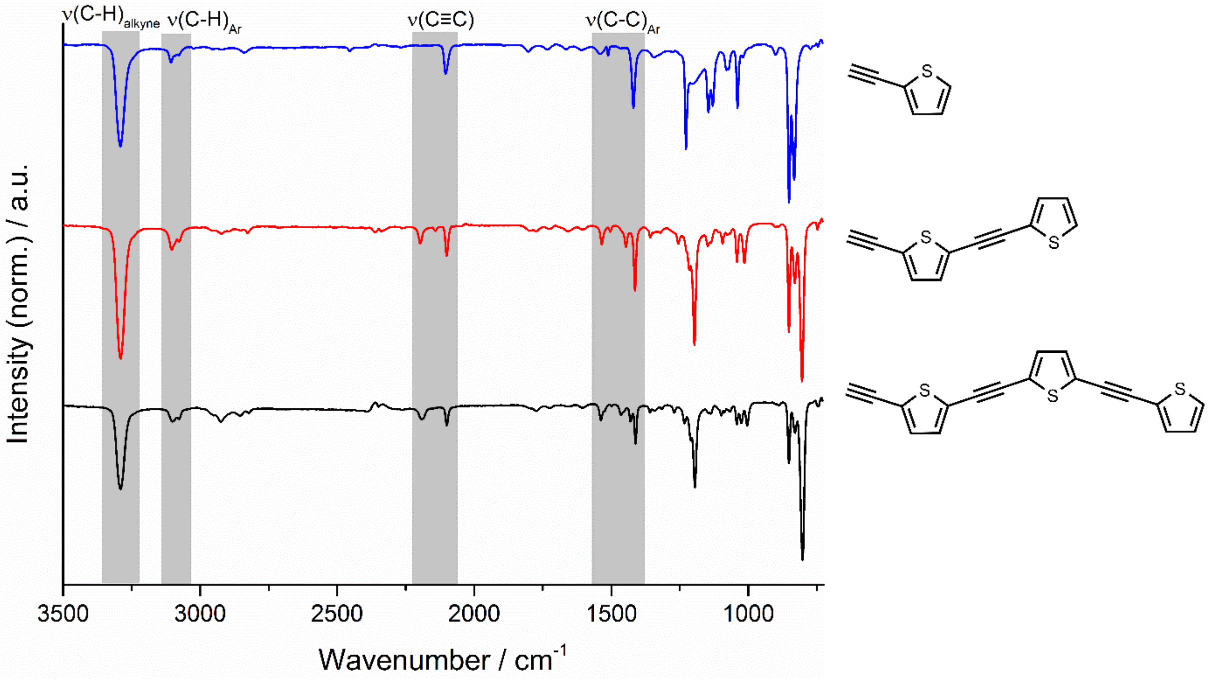


Fig.4-5 FTIR spectra of ethynylthiophene conjugative systems: ET-1 (blue), ET-2 (red), ET-3 (black)

Phenylacetylene and ethynylthiophene conjugative systems were obtained very precisely, evident from FTIR spectra. Alkynyl C≡C stretch and aryl C-H stretch were used as characteristic features to demonstrate that the modification was feasible after the terminal alkynyl groups were grafted onto the particle surface. This provides a good basis for the next step of surface modification of silicon nanoparticles.

Ultraviolet-visible Spectroscopy (UV-Vis)

Phenylacetylene conjugative systems

For PE-1 (black line in Fig. 4-6), the benzene ring forms a conjugation with carbon-carbon triple bond and the red shift is observed on the UV-Vis spectrum, at 240 nm – 250 nm. A strong absorption peak is also defined as the red shift at 260 nm – 280 nm, which is displayed from the characteristic bands and fine structure of the benzene ring.

Meanwhile, for the PE-2 and PE-3 systems, the conjugation systems further increase, and the UV absorption shifts to the long-wave direction more than that of phenylacetylene, and the absorption intensity increases.

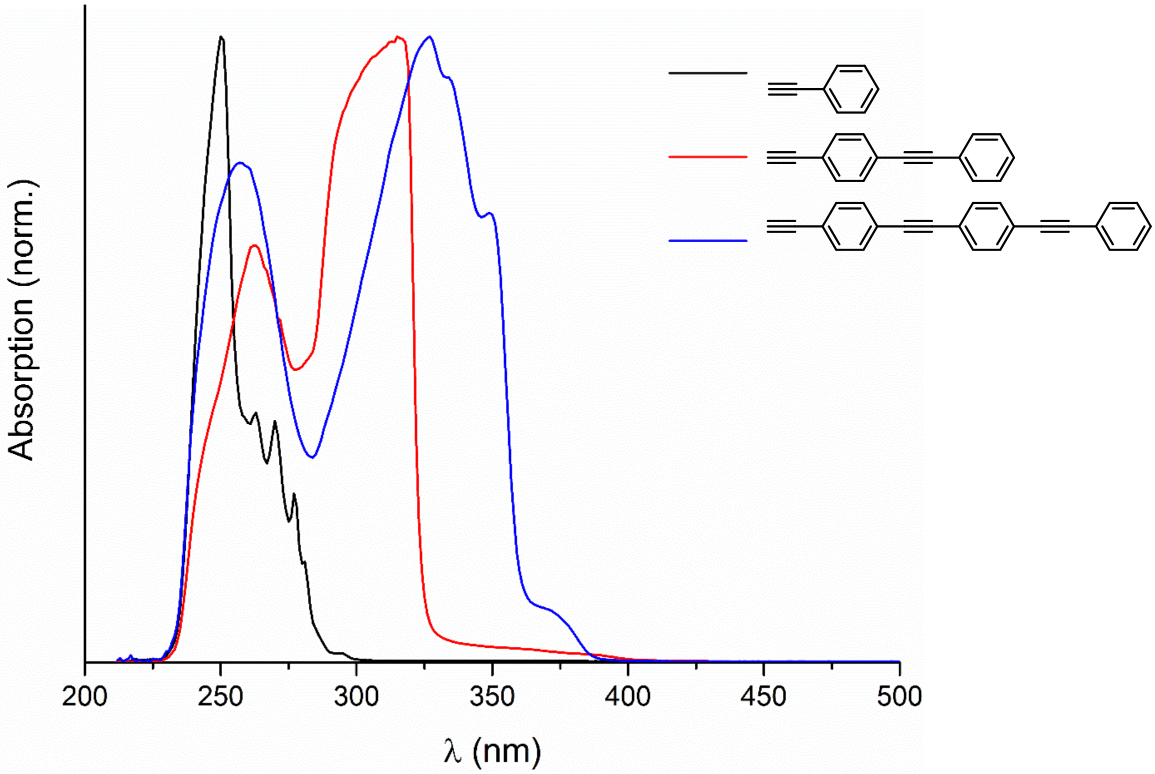


Fig.4-6 UV-Vis spectrum of phenylacetylene conjugative systems: PE-1 (black), PE-2 (red), PE-3 (blue)

Ethynylthiophene conjugative systems

From the UV-Vis spectrum (Fig. 4-7), the strong absorption peaks of thynylthiophene can be found at 230 nm – 290 nm. UV-Vis absorptions of ET-2 and ET-3 shift to the long-wave direction, which are positively correlated with their conjugation system.

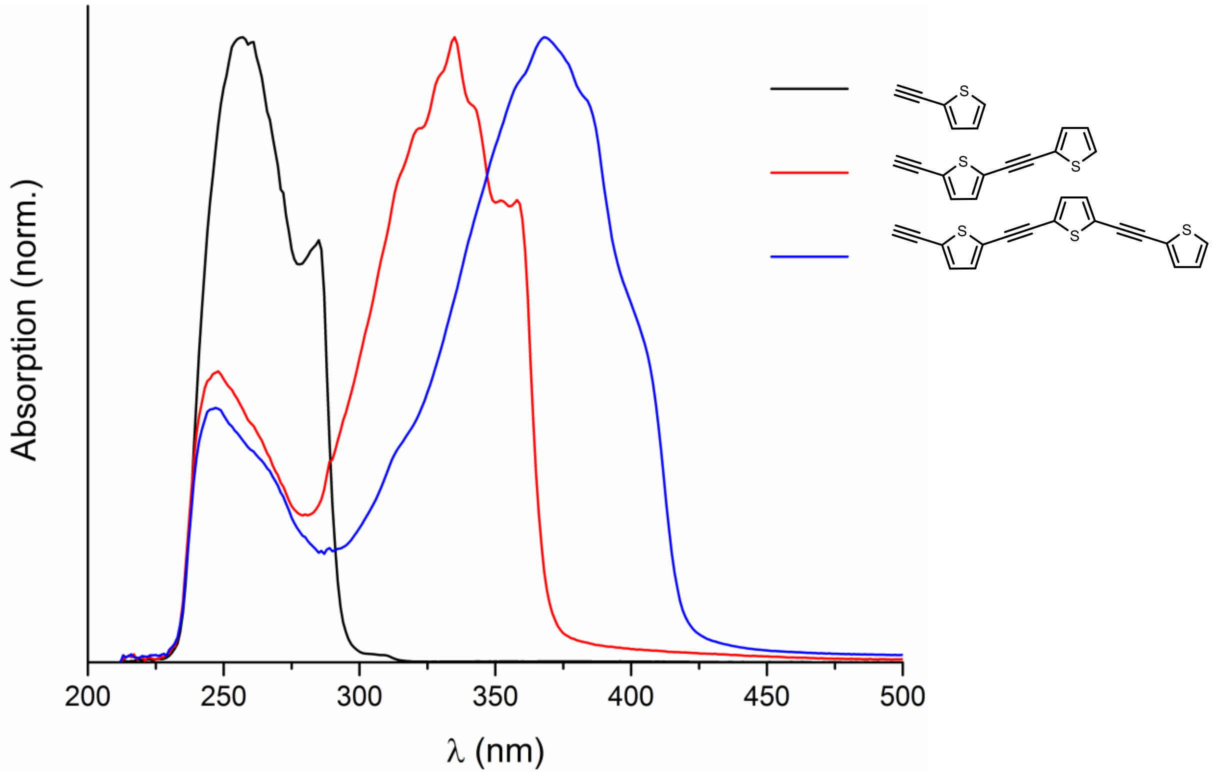


Fig.4-7 UV-Vis spectrum of ethynylthiophene conjugative systems: ET-1 (black), ET-2 (red), ET-3 (blue)

The ethynylthiophene conjugative systems and the phenylethyne conjugative systems have comparable UV-Vis absorption properties. The introduction of a co-chromophore in the thiophene ring produces a red shift of UV-Vis absorption. The electronegativity of the sulfur atom is similar to the electronegativity of the carbon atom, so it can form a conjugate with the carbon-carbon triple bond.

Photoluminescence Spectroscopy (PL)

Strongly photoluminescence substances usually have large π-π conjugated systems and rigid planar structures, which are the result of molecular rotation or groups that can cause fluorescence bursts.

The rigid structure of the molecule prevents the loss of energy due to vibration and rotation of the excited molecule, while the planar structure of the molecule allows the π electrons in the molecule to move and relax to lower energy fixed domain orbitals, both increase the chance of photoluminescence, resulting in an increase in photoluminescence emission intensity.

Phenylacetylene conjugative systems

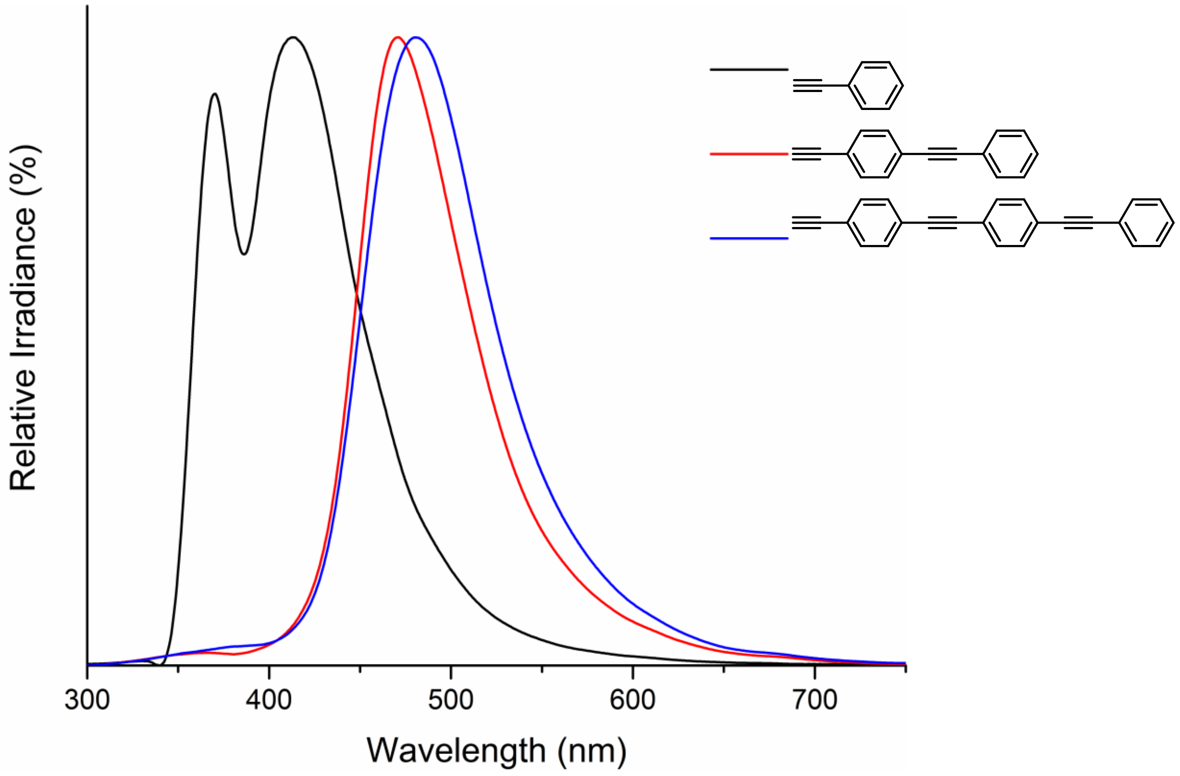


Fig.4-8 Photoluminescence spectrum of phenylacetylene conjugative systems: PE-1 (black), PE-2 (red), PE-3 (blue)

As shown in Fig. 4-8 and 4-9, all PL peak wavelength are located to the left of 600nm. Usually, the photoluminescence peak wavelength of pure SiNCs is located to the right of 600nm. So the PL results of conjugative systems make the following PL analysis of modified SiNCs clearer and simpler.

Ethynylthiophene conjugative systems

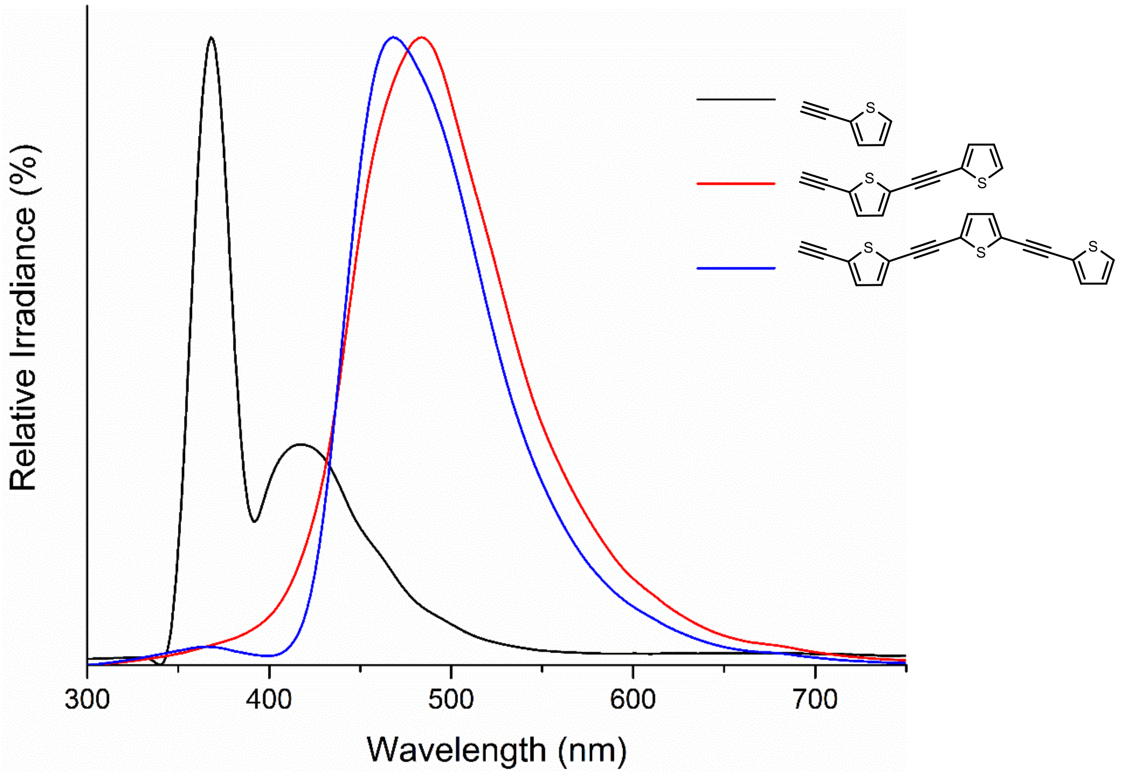


Fig.4-9 Photoluminescence spectrum of ethynylthiophene conjugative systems: ET-1 (black), ET-2 (red), ET-3 (blue)

4.1.3 Summary and Conclusion

Conjugated surface systems of similar structures can be easily obtained using Sonogashira coupling reaction and deprotection reaction. The synthesis of alkynyl end groups is evidenced by ^{1}H-NMR, ^{13}C-NMR spectroscopy, FTIR and UV-Vis. Photoluminescence demonstrates different peak wavelength than pure SiNCs.

The synthesis of conjugated systems is the cornerstone of surface modification of silicon nanoparticles. With these conjugated surface groups, the surface chemistry of silicon nanoparticles can be further enriched, and the properties of organic-inorganic hybrid materials will be further explored. PL peak wavelength

4.2 One-Step SiNCs Functionalization

4.2.1 Research Proposal and Experimental Route

In this part of the work, different alkynyl end systems were expected to be grafted onto the surface of the SiNCs. Photoluminescence was subsequently studied, and surface coverage was also required to be noted. Based on previous investigations, alkynyl end conjugated groups (obtained in chapter 4.1) were designed into the organolithium reagents, so in the next step they were directly grafted onto the surface of the SiNCs. After removing the organolithium reagents, the modified SiNCs were characterized.

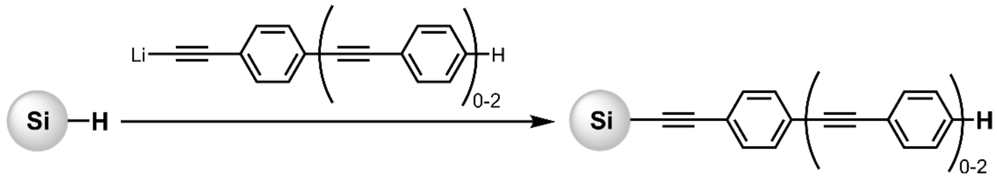


Fig.4-10 Functionalization SiNCs with phenylacetylene conjugative systems.

Hydrogen-terminated SiNCs were similarly modified with dodecene. The relevant results are elaborated together and compared.

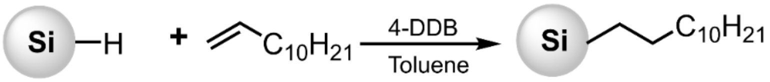


Fig.4-11 Functionalization SiNCs with 1-dodecene.

4.2.2 Results and Discussion of One-Step Functionalization Method

Fourier Transform Infrared Spectra (FTIR)

FTIR can be used to identify the surface functionalized SiNCs. In Fig. 4-12, for the dodecene-modified SiNCs, distinct alkyl peaks can be found at 3000 cm^{-1} - 2800 cm^{-1} and 1490 cm^{-1}, especially the sharp and strong peak at 3000 cm^{-1} - 2800 cm^{-1}. Meanwhile, around 2100 cm^{-1}, it shows a signal of Si-H stretching. There is slight oxidation occurring in the reaction, and the peak around 1100 cm^{-1} can be evidence of oxidation. The weak Si-H stretching proves that dodecene can modify the SiNCs very well.

In addition, the dodecene on the surface of the SiNCs is a soft and long-chain organic molecules, which enables the modified SiNCs to exhibit excellent dispersion (in toluene). So the dodecene surface group can be used as a comparison for the next steps.

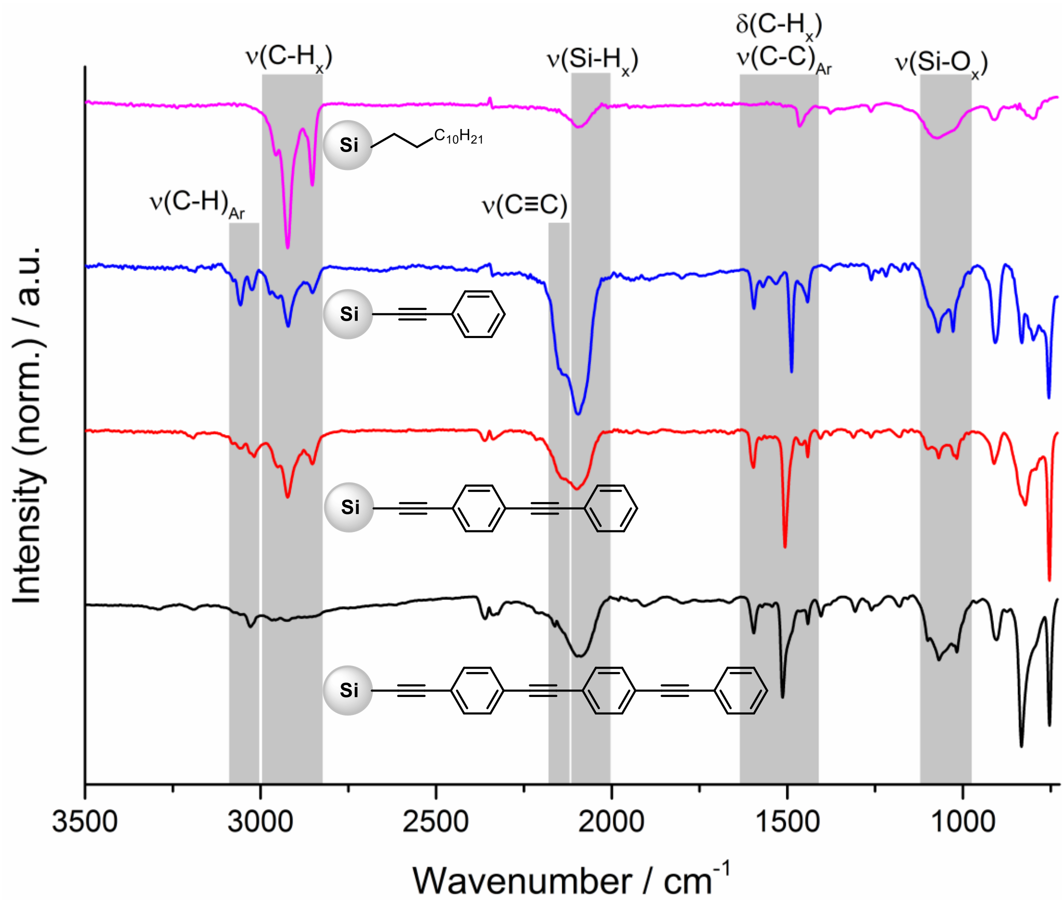


Fig.4-12 FTIR spectra of (pink) 1-dodecene, (blue) PE-1, (red) PE-2, (black) PE-3 functionalized SiNCs.

In contrast to the dodecene-modified SiNCs, the conjugative surface groups functionalized SiNCs show evidence of aromatic rings (C-H stretching) around 3050 cm^{-1}. The weak band at 2150 cm^{-1} imply the existence of asymmetric C≡C stretching in conjugative systems. Clear evidence of aromatic C=C stretching is confirmed at 1610 cm^{-1} - 1400 cm^{-1} which is considered typically for the phenyl groups. Slight oxidation on the surface of SiNCs occurs during the centrifugation and washing steps, which is hardly avoided.

Alkynyl end groups are designed to be organolithium reagents, and subsequently be grafted directly onto the SiNCs surface. The FTIR spectra illustrate the presence of alkynyl and aryl groups. Unfortunately, as the volume of surface groups increased (from PE-1 to PE-3), the dispersion of the modified SiNCs in organic solvents become worse, which had an impact on the following photoluminescence tests.

Photoluminescence Spectroscopy (PL)

With the photoluminescence spectra, the optical properties of the surface-modified SiNCs can be demonstrated. After functionalizing with 1-dodecene, the SiNCs show PL peak wavelength at ~737nm (Fig. 4-13), which is the base value for the SiNCs. Meanwhile, PE-1 and PE-2 functionalized SiNCs have peak wavelength redshifts of 48 nm and 53 nm, respectively, which indicate that the optical properties of the SiNCs are changed after the attachment of carbon-carbon triple bond conjugate groups on the SiNCs surface. Unfortunately, PE-3 functionalized SiNCs possess a larger conjugate group, implying that it has sterically more demanding, hence the nanoparticle surface coverage of PE-3 is low and the relative oxidation is high, which is manifested by the blueshift of the peak wavelength.

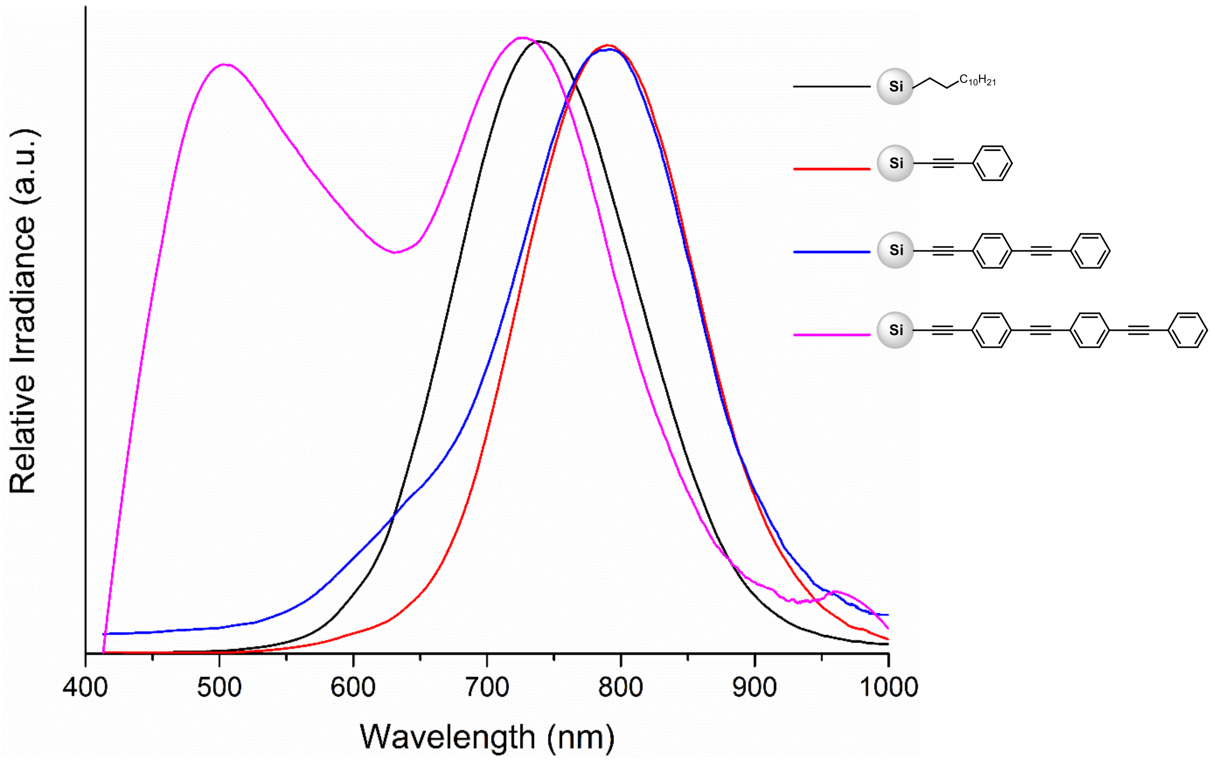


Fig.4-13 PL spectra of (black) 1-dodecene, (red) PE-1, (blue) PE-2, (pink) PE-3 functionalized SiNCs.

Surface Functionalization	PL(nm)	ΔPL(nm)
1-dodecene	737	/
PE-1	785	+48
PE-2	790	+53
PE-3	730	-7

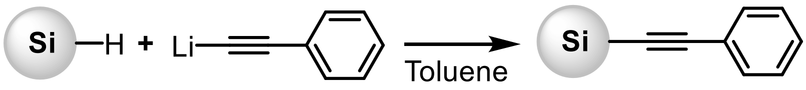
Table.4-1 Peak wavelength of functionalized SiNCs

Although the FTIR spectra demonstrated successful surface modification, the fact is that poor dispersion made photoluminescence testing difficult. Therefore the amount of organolithium reagents added, which can be considered as the concentration of organolithium reagents, should be investigated. Also the surface coverage was studied when comparing the addition of different concentrations of organolithium reagents.

In view of the above conjugate groups modification of SiNCs, two-steps modification method should be employed to improve surface coverage and reduce oxidation, and can be characted by thermogravimetric analysis (TGA). In the next step, a two-steps modification method will be used to treat the SiNCs.

4.2.3 Influence of Organometallic Reagents Concentration

A range of different concentrations of organolithium reagents were used to modify the SiNCs, to determine the effect of concentration on the functionalization of the nanoparticle surface. To simplify the experimental procedure, the phenylethylene functional group was chosen as the main modifying moiety.



Fourier Transform Infrared Spectra (FTIR)

After phenylethylene modification, FTIR shows highly comparable spectra. The aromatic groups, carbon-carbon triple bond, benzene ring characteristic peaks, Si-H, and oxidation peaks can be identified. The FTIR (Fig. 4-14) shows that the concentration of organometallic reagents has minimal effect on the modification process. The reason is, after surface functionalization, same grafted groups are obtained. Even with 0.2 mmol of surface groups, the desired FTIR spectra can be obtained, wastage of starting materials can be avoided.

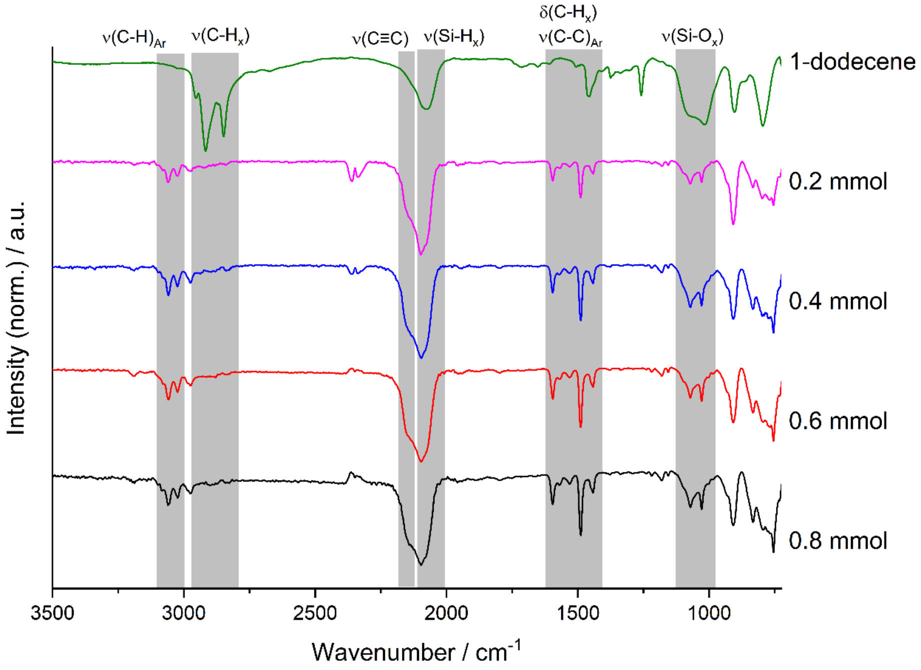


Fig.4-14 FTIR spectra of 1-dodecene and different amount of PE-1 functionalized SiNCs.

Thermogravimetric Analysis (TGA)

Qualitative studies of surface coverage can be characterised by TGA. For the same silicon nanoparticles functionalized with same surface groups: (a) if the mass loss is larger, proves that there are more surface groups and higher surface coverage; conversely, (b) if the mass loss is smaller, proves that there are fewer surface groups and lower surface coverage. In a similar way to the FTIR results, the four PE-1 functionalized SiNCs show an analogous mass loss (approximately 5%) in the TGA spectra (Fig. 4-15). Compared to the 1-dodecene modified silicon nanoparticles, the PE-d1 modified silicon nanoparticles still have a large amount of unreacted Si-H on the surface. Applying different amounts of surface groups did not help with surface coverage improvement.

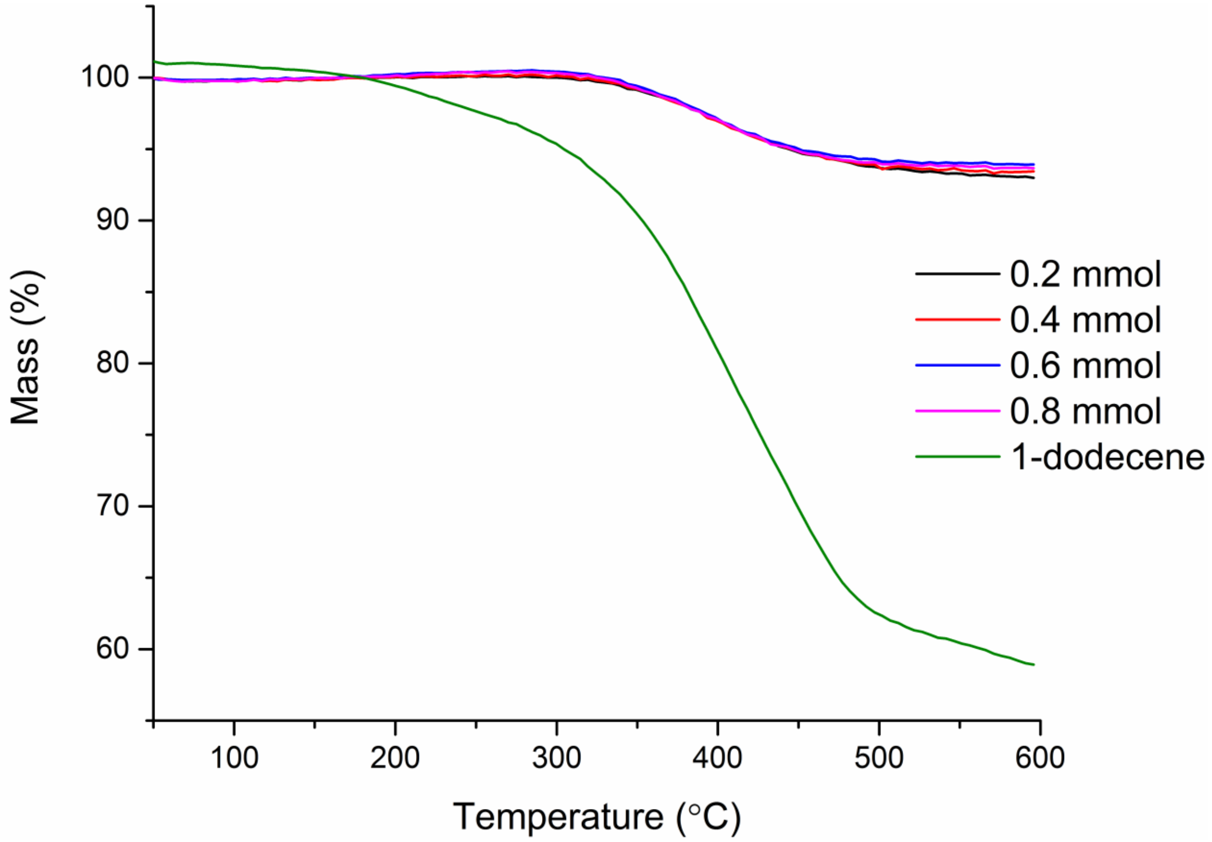


Fig.4-15 TGA analysis of 1-dodecene and different amount of PE-1 functionalized SiNCs.

Photoluminescence Spectroscopy (PL)

The PL spectra exhibit slightly different peak wavelengths (Fig. 4-16 black, red, blue and pink line), but in general, the differences are minor and the amount of organometallic reagents has minimal effects. In common, the emission wavelength is related to the specific surface moieties, or to the ground and excited states. An increase or decrease in surface coverage does not produce a change in the emission wavelength.

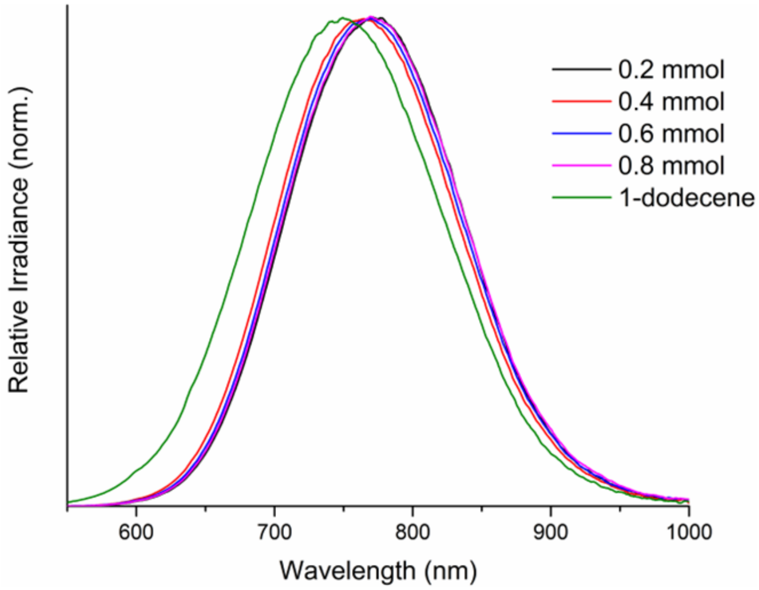


Fig.4-16 PL spectra of 1-dodecene and different amount of PE-1 functionalized SiNCs.

4.2.4 Summary and Conclusion

In this part of the study, alkynyl end conjugated groups were produced as organolithium reagents and modified onto the surface of the SiNCs. Subsequently the above modified SiNCs were tested. FTIR spectra demonstrated evidence of the presence of conjugated groups, with carbon-carbon triple bonds and aromatic groups being identified obviously. Benefiting from the direct attachment of terminal alkynes to the silicon nanoparticles, red shifts were noted in the photoluminescence spectra. The experimental doping amounts of organolithium reagents were also investigated. The results showed approximately the same, either in FTIR or photoluminescence. TGA demonstrated there was no significant relationship between the amount of conjugate groups grafted and the amount of organolithium reagents doped. The surface of the silicon nanoparticles needs to be further modified due to the poor dispersion and insufficient photoluminescence intensity of the nanoparticles found in the experiments.

4.3 Two-Steps SiNCs Functionalization

4.3.1 Research Proposal and Experimental Route

Large conjugate groups were modified to the surface of the SiNCs via organolithium reagents functionalization and remained the redshift of photoluminescence. However, modified SiNCs have a lower surface coverage and still have a large amount of active hydrogen on the surface, and therefore more susceptible to oxidation. In addition, the modified SiNCs are poorly dispersible in organic solvents, so secondary modification using easily soluble groups is used to improve surface coverage and increase dispersibility. In view of the above conjugate groups modification of SiNCs, two-steps modification method should be employed to improve surface coverage and reduce oxidation, and can be characted by thermogravimetric analysis (TGA). In the next step, a two-steps modification method will be used to treat the SiNCs.

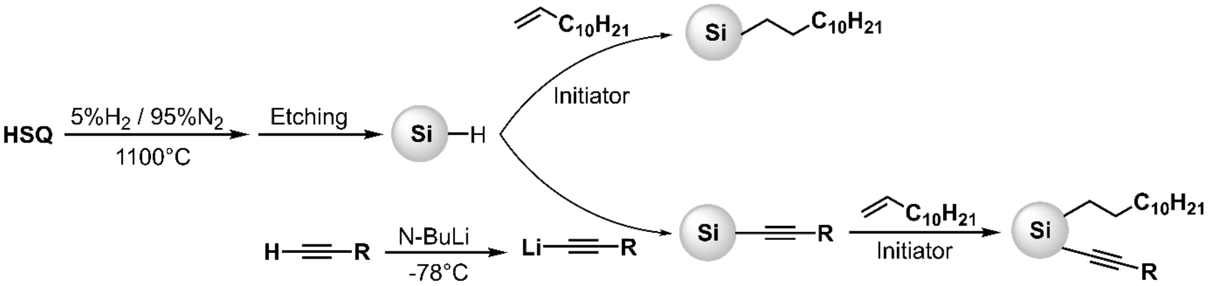


Fig.4-17 Scheme of two-steps SiNCs functionalization

1-Dodecene functionalized SiNCs are well dispersed in organic solvents (toluene) and exhibit a transparent liquid after dispersion. Moreover, after the SiNCs are grafted by large conjugate groups, a large amount of activated hydrogen is still present, so 1-dodecene is used to further modify the SiNCs. After the two-steps modification, the SiNCs theoretically become easily dispersible and the surface coverage is improved.

4.3.2 Results and Discussion of Two-Steps Functionalization Method (Phenylacetylene Conjugative Systems)

The conjugated SiNCs and toluene mixture are degassed to get an oxygen-free system. 1-dodecene is added to the complexes. After purification, the co-modified SiNCs were obtained .

Fourier Transform Infrared Spectra (FTIR)

FTIR spectra demonstrate obvious evidence of surface modified SiNCs. In Fig. 4-18, aryl C-H stretching can be found at 3100 cm^{-1} - 3020 cm^{-1}, and the peak wavelength (2150 cm^{-1}) implies the existence of asymmetric C≡C stretching of phenylacetylene. Around 2100 cm^{-1} and 1600 cm^{-1} - 1400 cm^{-1}, peak wavelength show the Si-H stretching and typical symbol of the phenyl group, respectively.

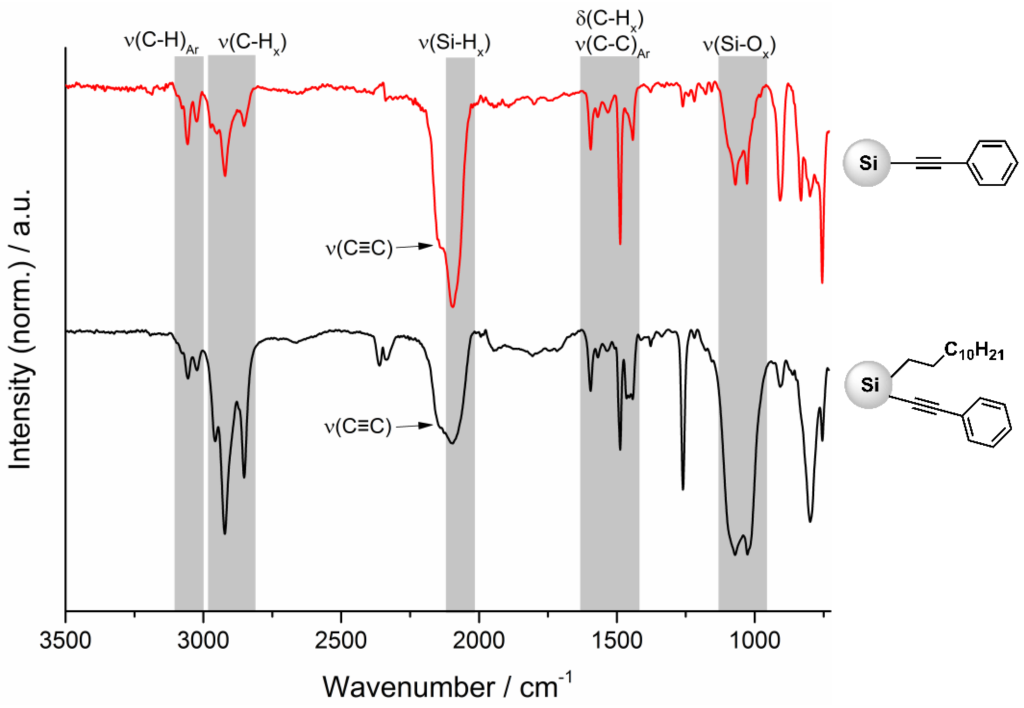


Fig.4-18 FTIR spectra of (red) PE-1 functionalized SiNCs, (black) PE-1 and 1-dodecene co-functionalized SiNCs.

From FTIR spectra, the aliphatic C-Hx stretching (3000 cm^{-1} - 2800 cm^{-1}) is significantly enhanced and the Si-H stretching (2100 cm^{-1}) is reduced after the second functionalization step, which indicates that the SiNCs surface is further modified.

For PE-2 functionalized SiNCs, the FTIR spectra (Fig. 4-19) are performed similarly to the PE-1 functionalized SiNCs. Aryl C-H stretching, asymmetric C≡C stretching, ta ypical symbol of the phenyl group can be found at 3100 cm^{-1} - 3020 cm^{-1}, 2150 cm^{-1}, 1600 cm^{-1} - 1400 cm^{-1}, respectively. After the second functionalization step, the enhanced alkyl peak and the reduced Si-H stretching indicate that the surface of SiNCs is further functionalized.

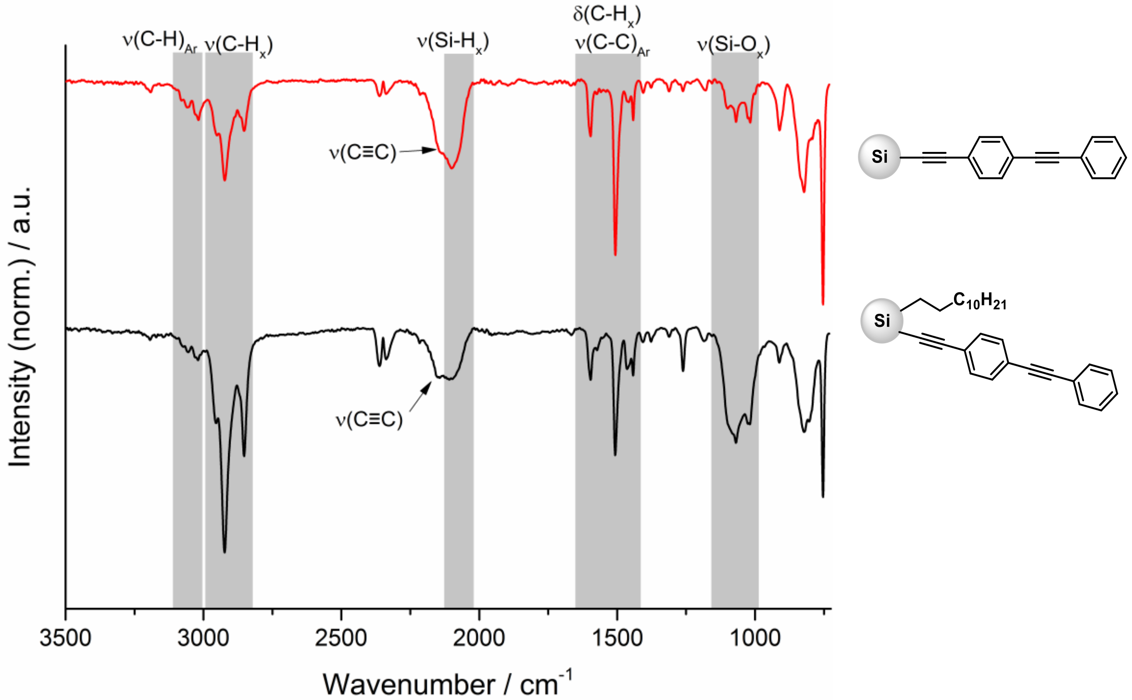


Fig.4-19 FTIR spectra of (red) PE-2 functionalized SiNCs, (black) PE-2 and 1-dodecene co-functionalized SiNCs.

For PE-3 functionalized SiNCs, even with a small amount of surface coverage, clear indications can be derived from FTIR spectra (Fig. 4-20). All characteristic peaks can be located in the spectra and the differences between before and after surface functionalization can be detected.

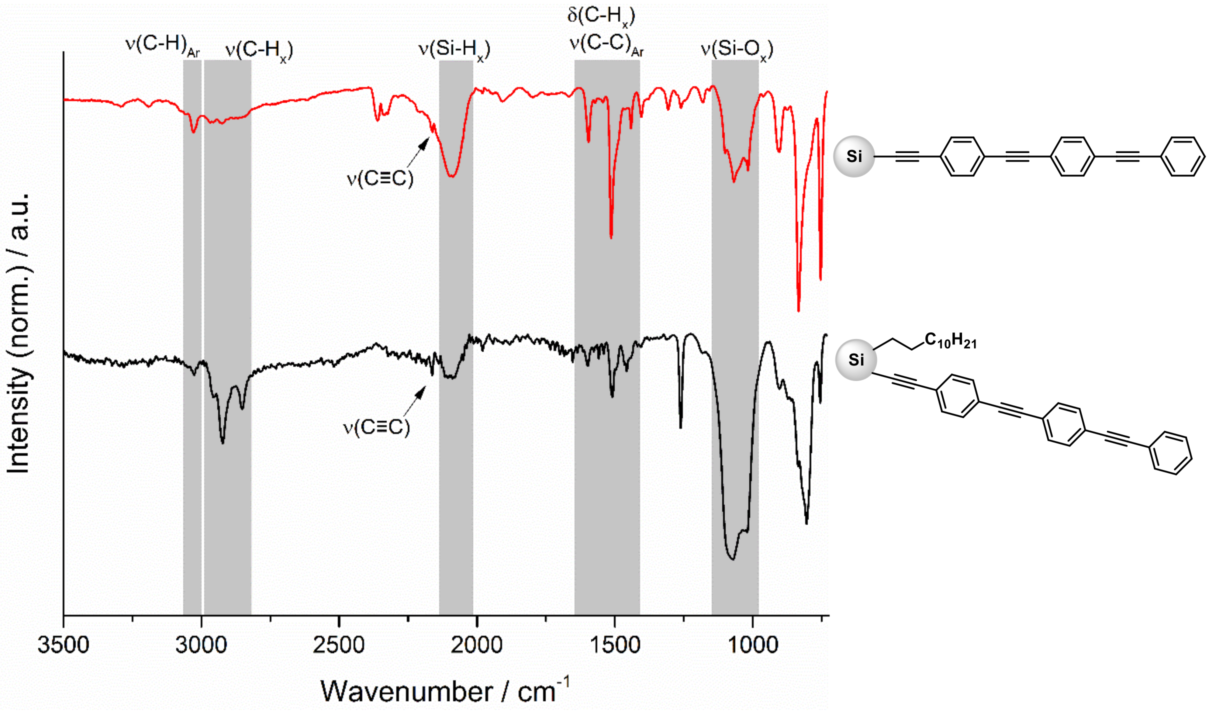


Fig.4-20 FTIR spectra of (red) PE-3 functionalized SiNCs, (black) PE-3 and 1-dodecene co-functionalized SiNCs.

Up to this point, the FTIR spectra give a clear indication that the PE conjugate systems can be modified onto the SiNCs surface via the organolithium approach, and by further hydrosilation reactions, 1-dodecene replaces the remaining Si-H bonds, thus the surface coverage is further enhanced. The two-steps approach does not have an effect on the surface conjugated groups, and the added 1-dodecene only occupies the unreacted Si-H, hence the signal of the alkyl group is enhanced in the FTIR spectra. Compared to the poor dispersion of the first-step product, the dispersion of the second-step product is enhanced, suggesting that 1-dodecene and conjugate groups co-functionalization is feasible. Based on the aforementioned results, the increase in surface coverage needs to be further determined.

Thermogravimetric Analysis (TGA)

The TGA analysis presumably indicates the amount of conjugative groups on the SiNCs surface. For the one-step functionalization product, only 8.1%, 5.3% and 4.6% mass loss were detected. Compared to the 40% mass loss of 1-dodecene functionalized SiNCs, the PE systems replace only a tiny fraction of the Si-H, and a large amount of Si-H is still left. This also results in SiNCs that are highly susceptible to oxidation.

After two-steps functionalization, the TGA presented mass loss of 23.8%, 14.8%, and 29.6% for PE-1, PE-2, and PE-3, respectively (Table. 4-2). These figures demonstrate that after the first step of modification, a large portion of the Si-H bond remains unreacted on the nanoparticle surface. However, after performing the second modification step, the mass loss increased further, demonstrating an improvement in surface coverage. The TGA analysis results are consistent with the FTIR spectra results, indicating that the SiNCs surface is optimized during this process.

	1-dodecene	PE-1	PE-2	PE-3
	Mass loss (%)	Mass loss (%)	Mass loss (%)	Mass loss (%)
One step functionalization	41.9	8.1	5.3	4.6
Two steps functionalization	/	23.8	14.8	29.6

Table.4-2 TGA analysis of different surface groups functionalized SiNCs

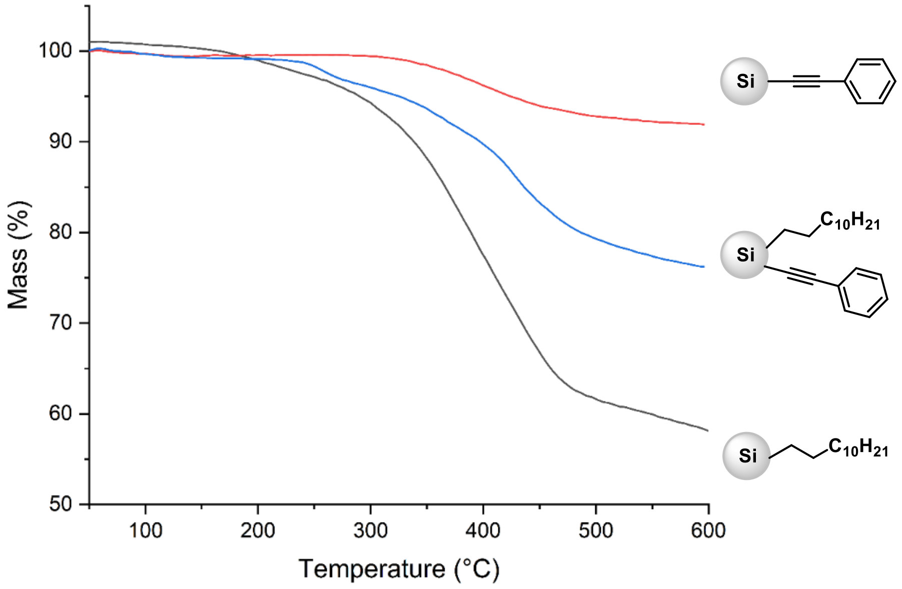


Fig.4-21 TGA analysis of (black)1-dodecene, (red) PE-1 functionalized SiNCs, (blue) PE-1 and 1-dodecene co-functionalized SiNCs.

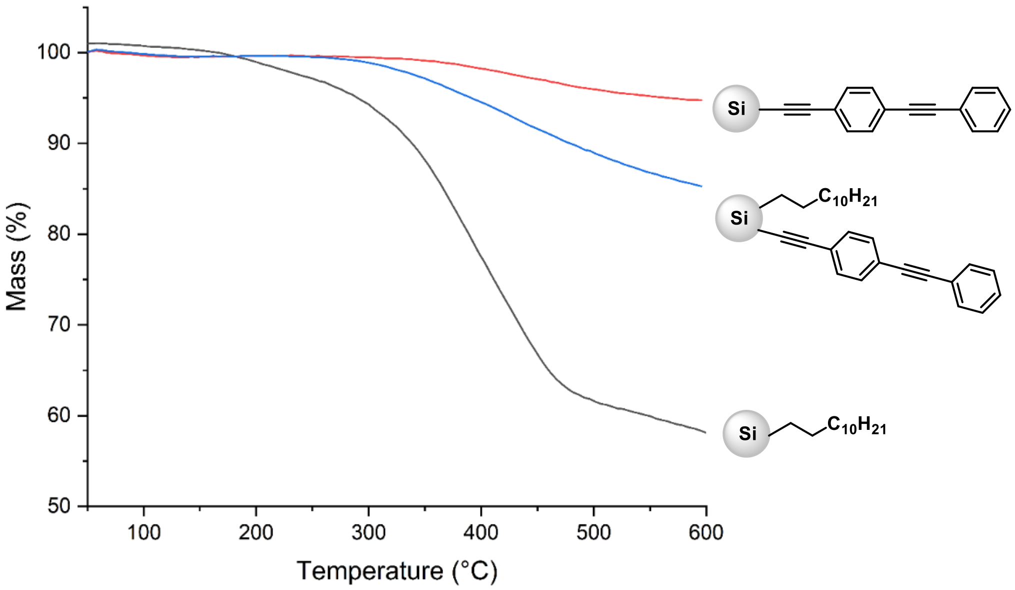


Fig.4-22 TGA analysis of (black)1-dodecene, (red) PE-2 functionalized SiNCs, (blue) PE-2 and 1-dodecene co-functionalized SiNCs.

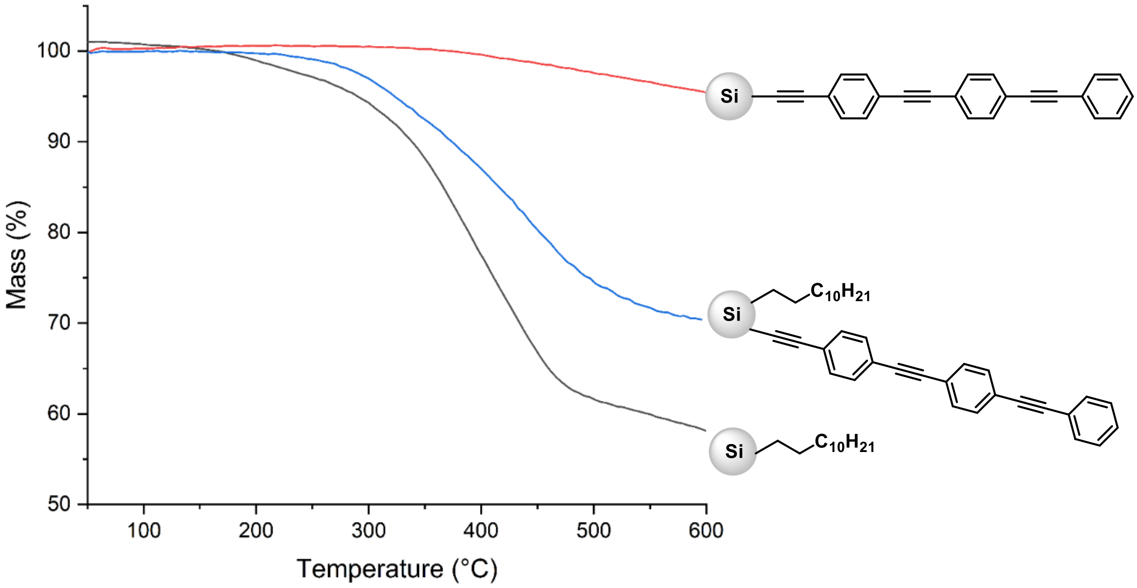


Fig.4-23 TGA analysis of (black)1-dodecene, (red) PE-3 functionalized SiNCs, (blue) PE-3 and 1-dodecene co-functionalized SiNCs.

Photoluminescence Spectroscopy (PL)

First of all, after the one-step modification, the PL red-shift of PE-1 and PE-2 systems are obviously to be detected. Due to the poor dispersion, PE-3 functionalized SiNCs doesn't show any red-shift and difficult to character. After the two-steps modification, the PL peak value of PE-1 and PE-2 systems were reduced by 8 nm and 3 nm (Table. 4-3), respectively, due to the increased surface oxidation during the second reaction step, which resulted in a blue shift. The SiNCs PL performance of the PE-3 system was improved after the second reaction step. The reasonable explanation is the very low surface coverage was obtained after the first step, but via second modification, PL recovered to a level similar to that of the 1-dodecene modified SiNCs.

Surface Functionalization	One step functionalization PL(nm)	Two step functionalization PL(nm)	∆PL(nm)
1-dodecene	737	/	/
PE-1	780	772	-8
PE-2	788	785	-3
PE-3	732	747	+15

Table.4-3 PL data of one step and two steps functionalized SiNCs

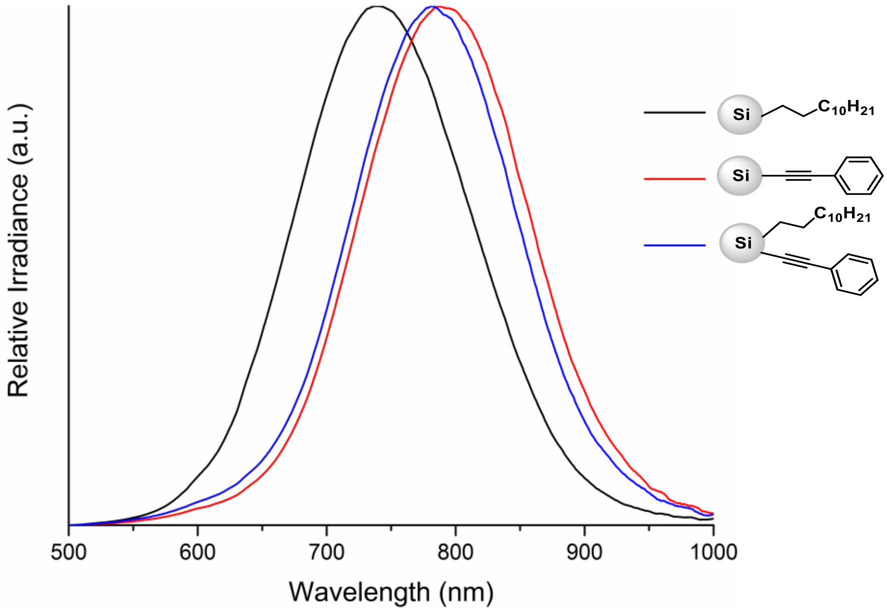


Fig.4-24 PL spectra of (black) 1-dodecene, (red) PE-1 functionalized SiNCs, (blue) PE-1 and 1-dodecene co-functionalized SiNCs.

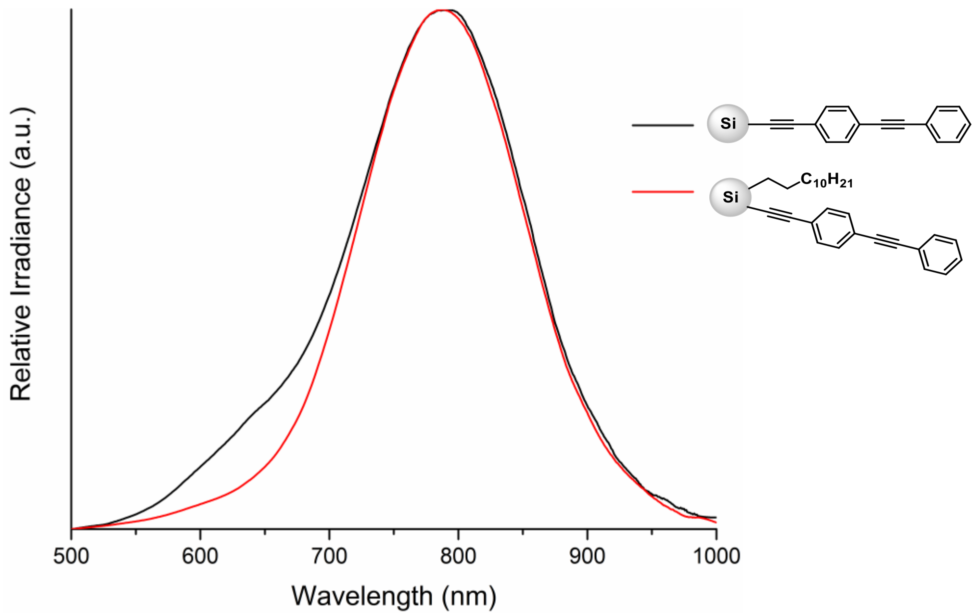


Fig.4-25 PL spectra of (red) PE-2 functionalized SiNCs, (black) PE-2 and 1-dodecene co-functionalized SiNCs.

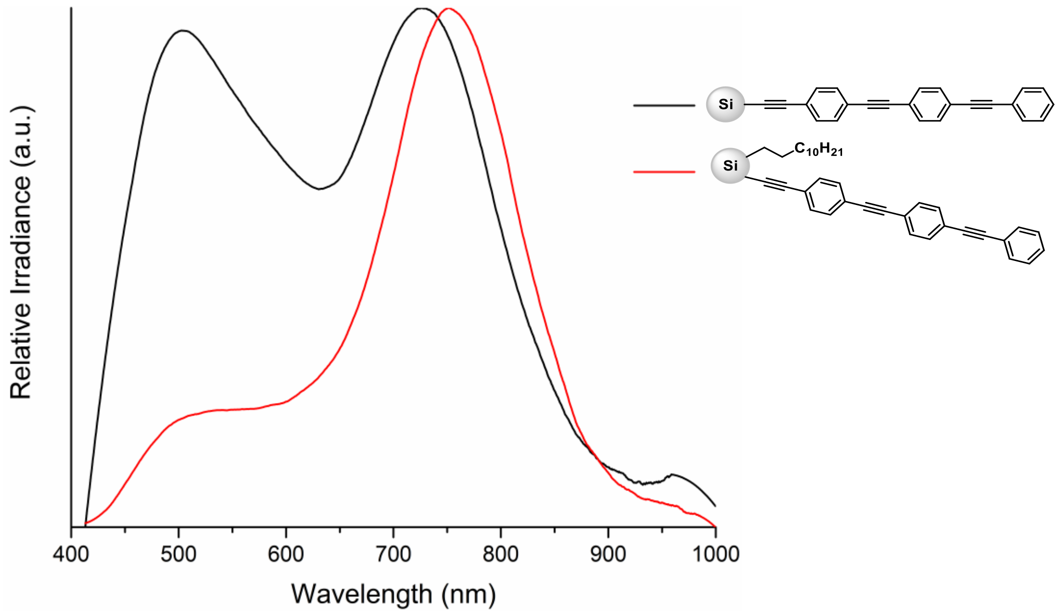


Fig.4-26 PL spectra of (black) PE-3 functionalized SiNCs, (red) PE-3 and 1-dodecene co-functionalized SiNCs.

For the PE systems, the photoluminescence of the SiNCs is preserved for both one-step and two-steps modifications. And for PE-1 and PE-2, the redshift is preserved, which provides the possibility for the photoluminescence application of SiNCs modified with large conjugate groups. The above characterisation results elucidate that a two-steps modification approach is achievable, thus a wider range of surface moiety species is designed to functionalize the SiNCs. In the next step, conjugated ethynylthiophene groups will be modified to the SiNCs surface.

4.3.3 Results and Discussion of Two-Steps Functionalization Method (Ethynylthiophene Conjugative Systems)

Aromatic ring materials have many properties that are affected by electrons and their alignment[114]. Thiophene is favored for applications in materials chemistry and drug design due to its electron-rich aromatic ring[115]. In the effort to enrich the surface groups of silicon nanoparticles and potential applications of doping in conductive polymer, series of thiophene groups were designed, synthesized and grafted onto the surface of silicon nanoparticles.

And the ETs functionalized SiNCs are aimed to improve the Seebeck coefficients of PEDOT:PSS by doping with SiNCs. Similarly, a two-steps modification method was used to reduce oxidation.

Fourier Transform Infrared Spectra (FTIR)

FTIR spectra can be used to identify the surface-functionalized SiNCs. First, for the ethynylthiophene-modified nanoparticles, aromatic C-H stretching can be found at 3050 cm^{-1}, and asymmetric C≡C stretching in the conjugative system can be found at 2150 cm^{-1} after the first functionalization step (red line in Fig.4-27).

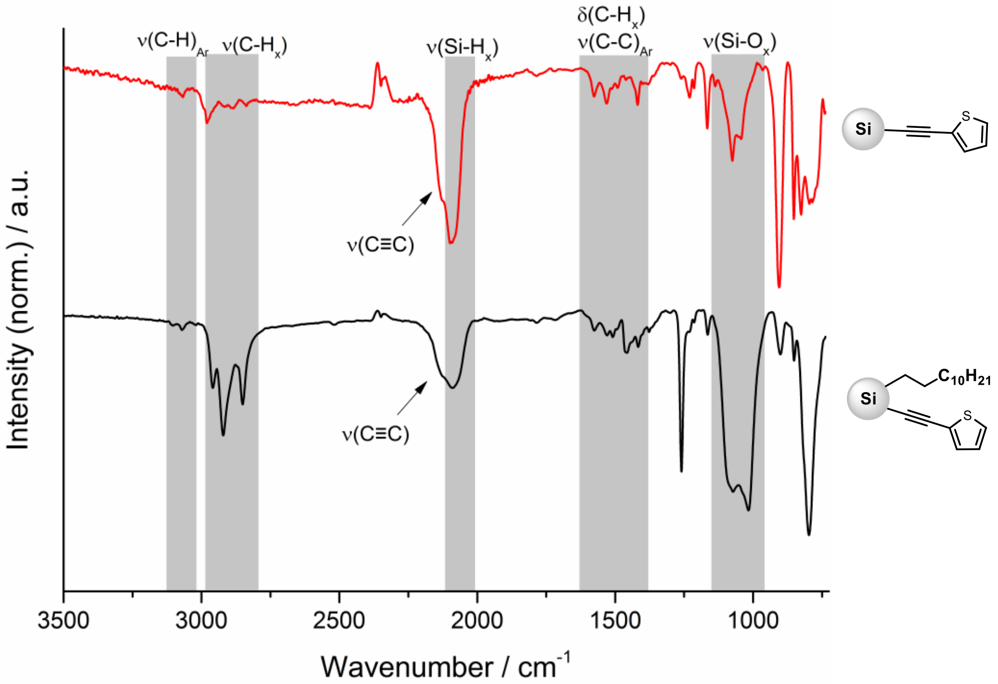


Fig. 4-27 FTIR spectra of (red) ET-1 functionalized SiNCs, (black) ET-1 and 1-dodecene co-functionalized SiNCs.

The latter band is present as a shoulder next to the Si-H band at approximately 2100 cm^{-1}, which shows that functionalization is not complete. These pieces of evidence prove the existence of the ethynylthiophene conjugate group attached to SiNCs. After the second modification step with 1-dodecene (black line in Fig. 4-27), the alkyl stretching was significantly enhanced at 3000 cm^{-1} - 2800 cm^{-1}, while the number of Si-H bonds was reduced, which clarified that the nanoparticle surface was further covered.

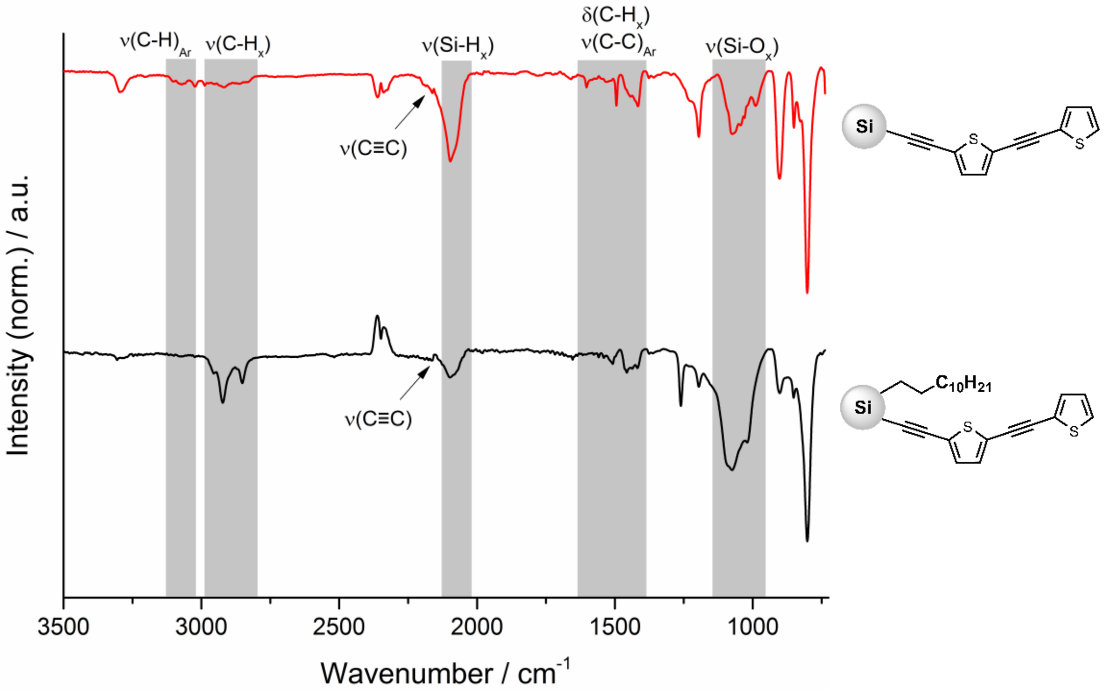


Fig. 4-28 FTIR spectra of (red) ET-2 functionalized SiNCs, (black) ET-2 and 1-dodecene co-functionalized SiNCs.

ET-2 and ET-3 conjugative systems presented similar results: Weak aromatic C-H stretching and asymmetric C≡C stretching in the conjugative system were observed in the FTIR spectra (red lines in Fig.4-28 and Fig.4-29), meanwhile after the second step of the surface modification, alkyl C-H stretching was significantly enhanced and Si-H stretching is reduced. Further surface oxidation represented by Si-O-Si bands at approximately 1050 cm^{-1} could not be avoided in all three cases.

The ethynylthiophene systems exhibit a similar FTIR performance to the phenylacetylene systems, with both C≡C stretching and aryl groups could be found a position of assignment. The co-functionalization of SiNCs by alkynyl end aryl and dodecene is successfully achieved.

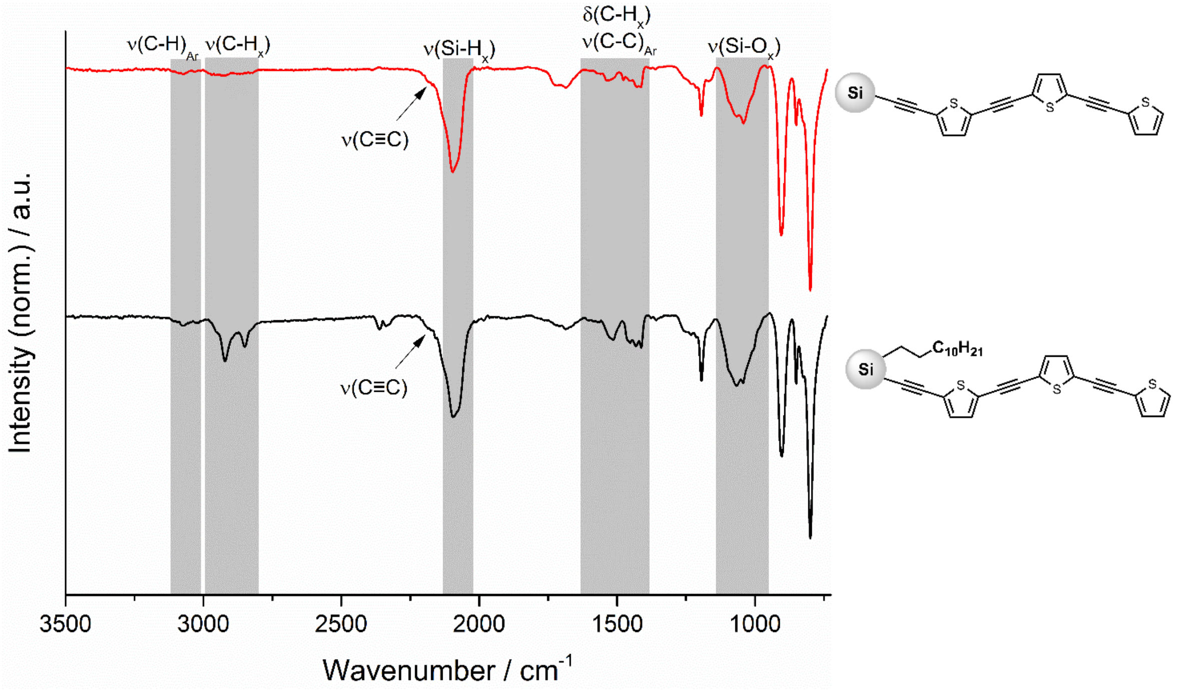


Fig.4-29 FTIR spectra of (red) ET-3 functionalized SiNCs, (black) ET-3 and 1-dodecene co-functionalized SiNCs.

Thermogravimetric Analysis (TGA)

The TGA data show that the surface coverage of SiNCs was low after one-step modification, 5.3%, 8.1%, and 4.6% for ET-1, ET-2, and ET-3 systems, respectively (Table. 4-4). After secondary modification using 1-dodecene, the surface coverage was greatly increased, 17.4%, 19.8, and 8.5 for ET-1, ET-2, and ET-3 systems, respectively.

	ET-1 Mass loss (%)	ET-2 Mass loss (%)	ET-3 Mass loss (%)
ET functionalization	5.3	8.1	4.6
ET-dodecyl co-functionalization	17.4	19.8	8.5

Table.4-4 TGA analysis of SiNCs functionalized with different conjugated ethynylthiophenes.

For all three surface moieties, the one-step modification approach does not significantly improve the surface coverage, as derivefrom the TGA, where only a small fraction of the Si-H bonds are replaced. Since dodecene is a straight-chain organic material, it is softer and more susceptible to being grafted onto the surface of the particles, thus showing more mass loss after the second steps of modification.

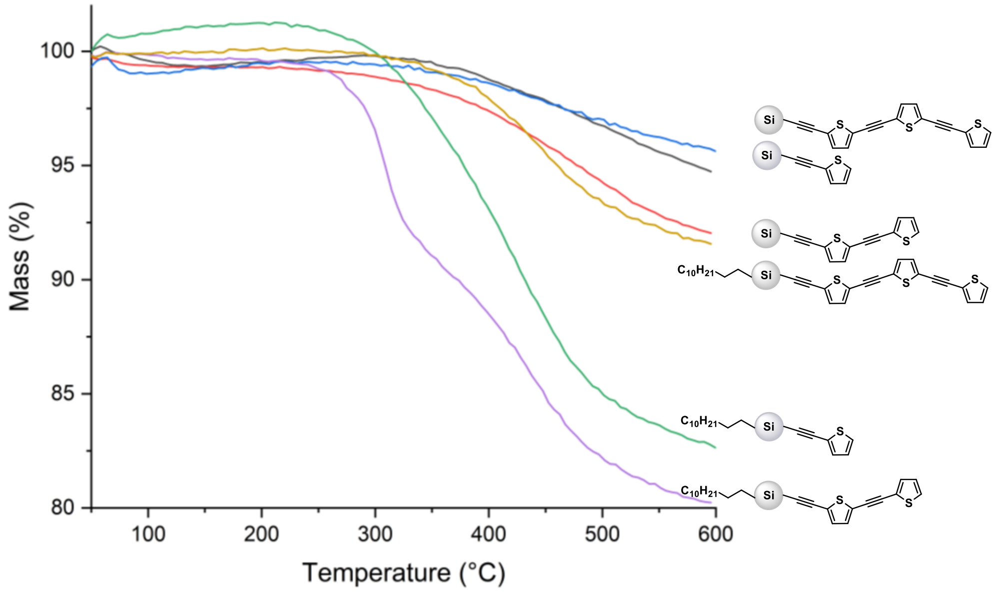


Fig.4-30 TGA analysis of SiNCs functionalized with different conjugated ethynylthiophenes.

Photoluminescence Spectroscopy (PL)

Compared to 737 nm emission maximum of 1-dodecene functionalized SiNCs, ET-1 functionalized SiNCs exhibit red-shift from photoluminescence wavelengths. After the secondary modification, the liquid is more transparent, indicates a further enhancement of its dispersion, thus the photoluminescence intensity is significantly enhanced. After normalization, the wavelength peak does not change significantly, indicating a invisible effect of the second modification step.

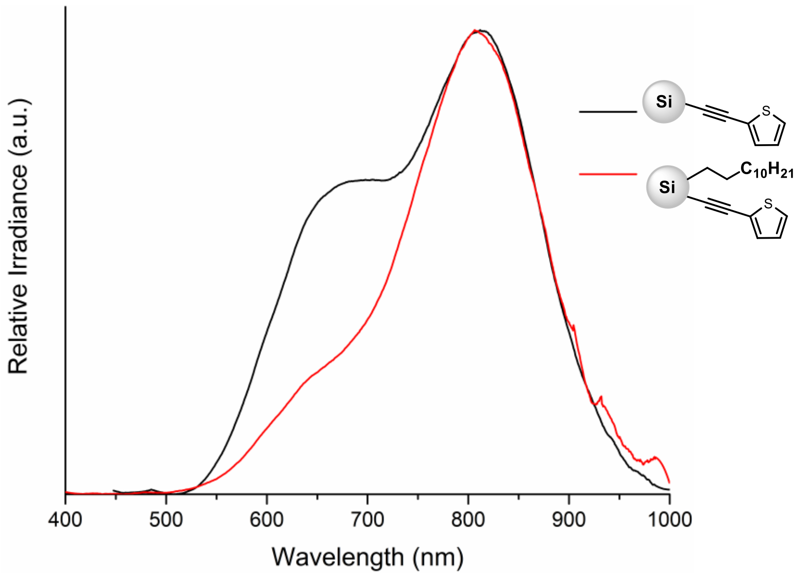


Fig.4-31 PL spectra of (black) ET-1 functionalized SiNCs, (black) ET-1 and 1-dodecene co-functionalized SiNCs.

Due to the poor dispersibility of ET-2 and ET-3 systems in organic solvents, their photoluminescence intensities are extremely feeble, and the PL spectra after normalization are significantly dissimilar so they are not sufficient as a reference. Accordingly, the surface chemistry should be further investigated for these two systems.

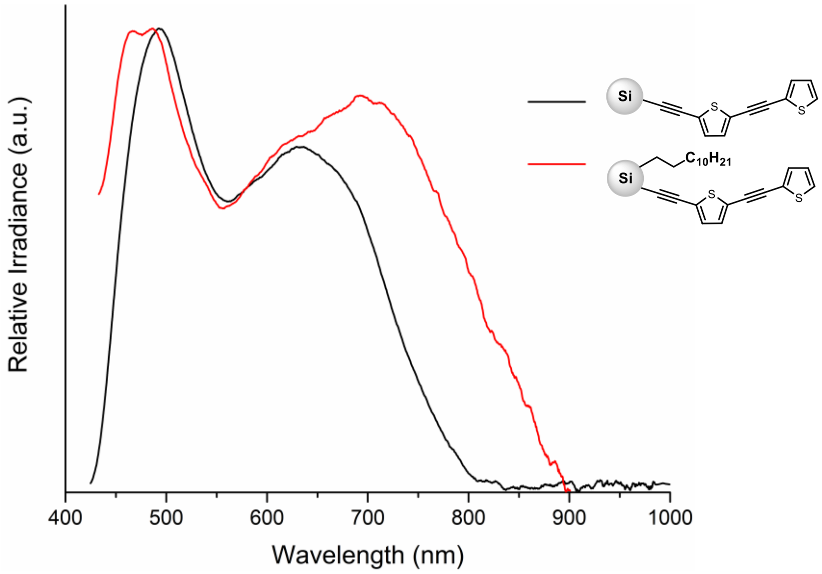


Fig.4-32 PL spectra of (black) ET-2 functionalized SiNCs, (black) ET-2 and 1-dodecene co-functionalized SiNCs.

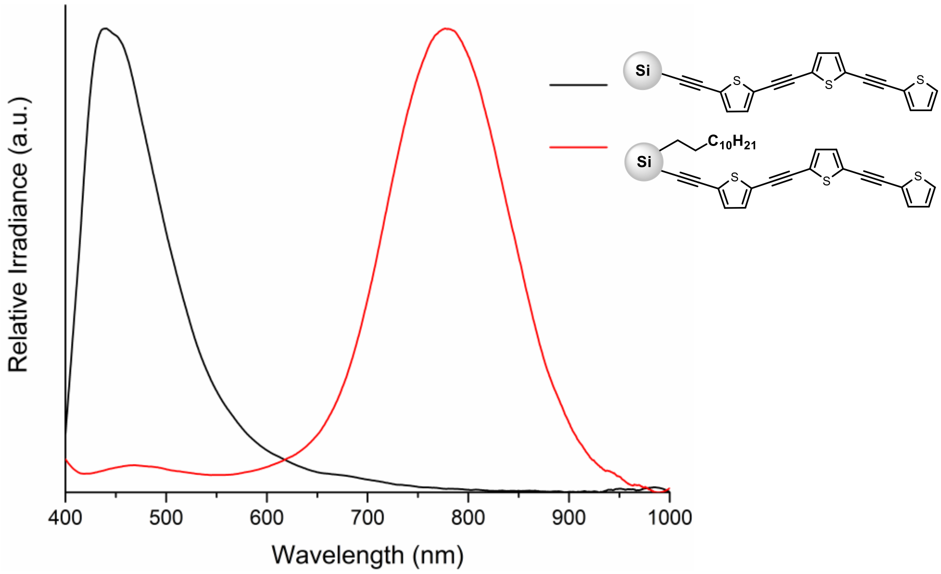


Fig.4-33 PL spectra of (black) ET-3 functionalized SiNCs, (black) ET-3 and 1-dodecene co-functionalized SiNCs.

4.4 Summary and Conclusion

By utilizing the organolithium reagents method, the conjugated groups can be easily modified onto the surface of silicon nanoparticles while preserving the carbon-carbon triple bond, PL red-shift is produced. The method provides a role model for the surface modification of nanoparticles by large conjugated systems. Meanwhile, large conjugated molecules are more difficult to lithiate; the nanoparticles modified with large conjugated molecules have low surface coverage, which easily leads to oxidation and poor dispersion in the solution. In addition, the application of different concentrations of organolithium reagents did not show significant differences in FTIR, TGA, and photoluminescence, which indicates that the amount of organolithium reagents did not adversely affect surface modification.

In order to increase the surface coverage of nanoparticles and optimize the solvent dispersion, a two-steps modification method can serve the purpose well. Increasing the surface coverage of silicon nanoparticles and optimizing the solvent dispersion are the goals, which can be well achieved by the two-step functionalization method. Phenylacetylene conjugative systems functionalized SiNCs can be modified using 1-dodecene. FTIR shows a decrease in the number of Si-H bonds on the surface of SiNCs, along with an increase in the intensity of the alkyl peaks and retention of the conjugated groups. TGA indicate an additional mass loss after the second step modification and a corresponding increase in the surface coverage. PL emission maximum did not have a major effect.

The two-step modification method can be extended to the ethynylthiophene conjugative systems. For ET-1, the FTIR spectra demonstrate that the conjugative group can be well modified onto the SiNCs surface, while the co-functionalization is followed by a further increase in the SiNCs surface coverage and a decrease in the number of Si-H bonds. A similar conclusion can be drawn from the TGA spectra, where the weight loss of SiNCs increases after co-functionalization. For its photoluminescence performance, the peak wavelengths of the two experimental results do not change significantly, and the co-functionalization don does not change its photoluminescence performance. For ET-2 and ET-3, the IR spectra exhibit difference before and after the second functionalization step, corresponding TGA spectra show a mass loss. The weak dispersion leads to the poor performance of their photoluminescence, which is a direction that can be further explored.

5. SiNCs/PEDOT:PSS Heterogeneous Materials

5.1 PEDOT:PSS Materials Doping with ET-1 Functionalized SiNCs

Thermoelectric (TE) materials are functional materials that use the migration motion of carriers within a solid material to directly convert thermal and electrical energy. One of the uses of thermoelectric materials is thermoelectric power generation devices[116], and has the advantages of no transmission parts, no noise, and high reliability[117]. The figure of merit (ZT) is usually used to evaluate the performance of thermoelectric materials, which is expressed as $ZT=S2\sigma T/\kappa$, where σ is the conductivity, S is the Seebeck coefficient (also known as thermoelectric power), κ is the thermal conductivity, and T is the absolute temperature[118].

Poly(3, 4-ethylenedioxythiophene:polystyrene sulfonate) (PEDOT:PSS) is used as one of the most common organic thermoelectric materials[119].The inherent thermal conductivity of PEDOT:PSS is lower than that of conventional thermoelectric materials. PEDOT:PSS consists of positively charged conjugated PEDOT chains and negatively charged PSS chains, where the PEDOT chains are attached to the PSS chains through Coulombic force interactions. Compared with other organic thermoelectric materials, PEDOT:PSS has the advantages of good thermal stability, low thermal conductivity, high electrical conductivity and high mechanical flexibility[120].

However, further improving the thermoelectric performance of PEDOT:PSS has been a great challenge. In order to achieve this goal, the selection of suitable methods to treat PEDOT:PSS is one of the current research directions. The addition of PEDOT:PSS to low-dimensional inorganic materials with good thermoelectric performance constitutes organic-inorganic nanocomposites to obtain thermoelectric optimum values comparable to those of inorganic materials[121]. SiNCs have high Seebeck coefficient and hence are designed to be doped into PEDOT:PSS. As the hydrogen-terminated SiNCs are susceptible to oxidation, they need to be functionalized before doping.

General information

The results presented in this chapter were developed in the collaboration with Suo Tu (Prof. Dr. Peter Müller-Buschbaum, Chair for Functional Materials, Technical University of Munich). Unless noted otherwise, all commercial reactants and catalysts were purchased from Sigma-Aldrich and used directly without further purification. Dry THF, toluene, and diethyl ether were obtained from an MBraun SPS 800 solvent purification system. N-butyllithium was bought as a 2.5 M solution in hexane. FTIR spectra were measured with a Bruker Vertex 70 FTIR using a Platinum ATR from Bruker.

Unless noted otherwise, the Synthesis of hydrogen silsesquioxane (HSQ), preparation of SiNC/SiO_2 nanocrystals composite, SiNC/SiO_2 composite etching time definition, and SiNCs functionalization are the same as for the above functionalization methods (refer to chapter 4.2).

PEDOT:PSS/SiNCs-ET-1 composite films were prepared by spin-coating as shown in Fig.5-1.

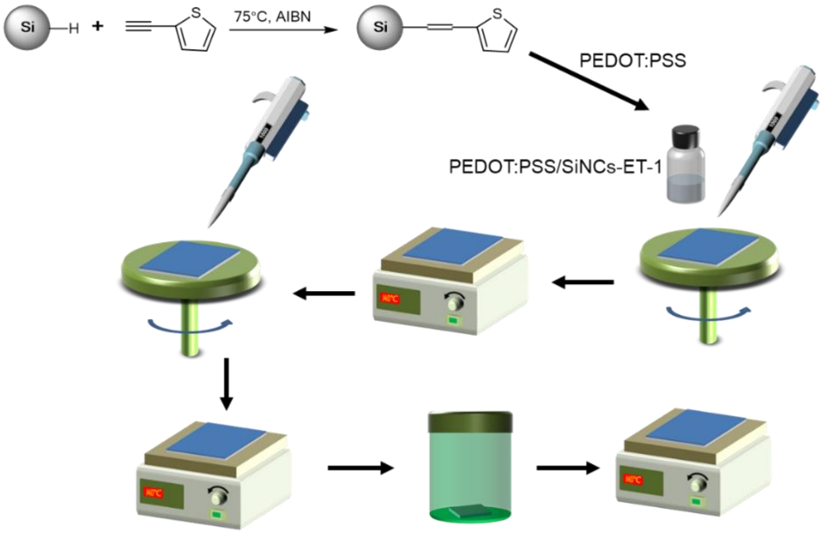


Fig.5-1 Schematics on deposition process of PEDOT:PSS/SiNCs-ET-1 composite films.

In Fig.5-2, GIWAXS patterns of the composite films show reflections at (100) and (200) which are assigned to PEDOT. The PEDOT and PSS chains are alternately arranged inside the film along the out-of-plane direction. The first broad ring corresponds to reflections arising from amorphous PSS regions which are randomly distributed in the film. The second broad ring, an intense peak, corresponds to π−π stacking of PEDOT chains. It is evident that the PEDOT chains are well connected by the removal of PSS. It can accompany by templating effect. Even the pure PEDOT: PSS thin films exhibit similar scattering patterns without any strong diffuse scattering from SiNCs. Doping SiNCs-ET-1 is favorable for PEDOT:PSS film, and DMSO treatment is also intensive.

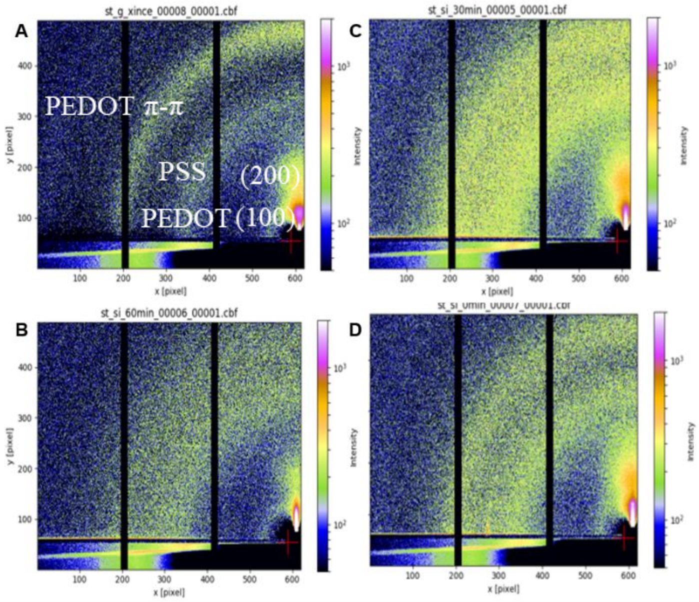


Fig.5-2 The GIWAXS pattern of PEDOT:PSS films: (A) PEDOT:PSS film; (B) PEDOT:PSS/SiNCs-ET-1 film; (C) DMSO vapor treated PEDOT:PSS/SiNCs-ET-1 film for 30 minutes; (D) DMSO vapor treated PEDOT:PSS/SiNCs-ET-1 film for 60 minutes

Seebeck Coefficient

Seebeck coefficients of PEDOT:PSS systems doped with different concentrations of SiNCs-ET-1 (0 to 40 wt%) were determined in order to identify the effect of doping amount on the coefficients.

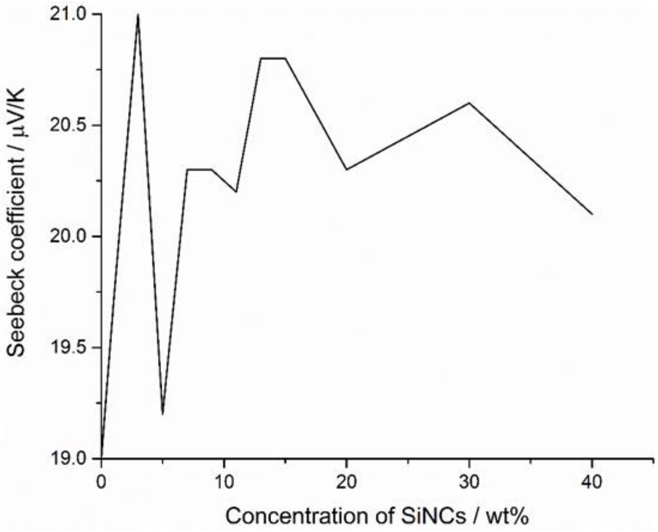


Fig.5-3 The plot of Seebeck coefficient

Fig.5-3 shows that the obtained Seebeck coefficients of SiNC-doped films are in a range of 19 to 21 μV/K and thus do not depend on the SiNC-ET-1 concentration. Additionally, the Seebeck coefficient of neat PEDOT:PSS does not differ significantly from those of doped films. In order to obtain higher values of the Seebeck coefficient, the surface groups of the SiNCs will be optimized. The polymer behaves as a *p*-type semiconductor; therefore, p-type silicon nanoparticle semiconductors will be studied in the following chapter.

5.2 PEDOT:PSS Materials Doping with 1H,1H,2H-perfluoro-1-decene Functionalized SiNCs

Strong electron-absorbing groups are attached to the nanoparticle surface in anticipation of increased electrical conductivity, which is kind of *p*-type semiconductor. Therefore, 1H,1H,2H,2H-perfluoro-1decene is used as ligand.

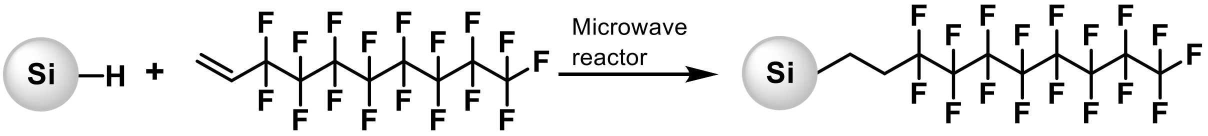


Fig.5-4 Functionalization SiNCs via microwave reactor.

Fourier Transform Infrared Spectra (FTIR)

FTIR spectra confirm the successful functionalization of SiNCs. In Fig.5-5, weak C-H stretching can be found at 2950 cm^{-1}, and Si-H stretching can be found at 2100 cm^{-1}. Due to functionalization with 1H,1H,2H-perfluoro-1-decene, strong bands in the region from 1250 cm^{-1} to 1100 cm^{-1} appear which are assigned to C-F stretching.

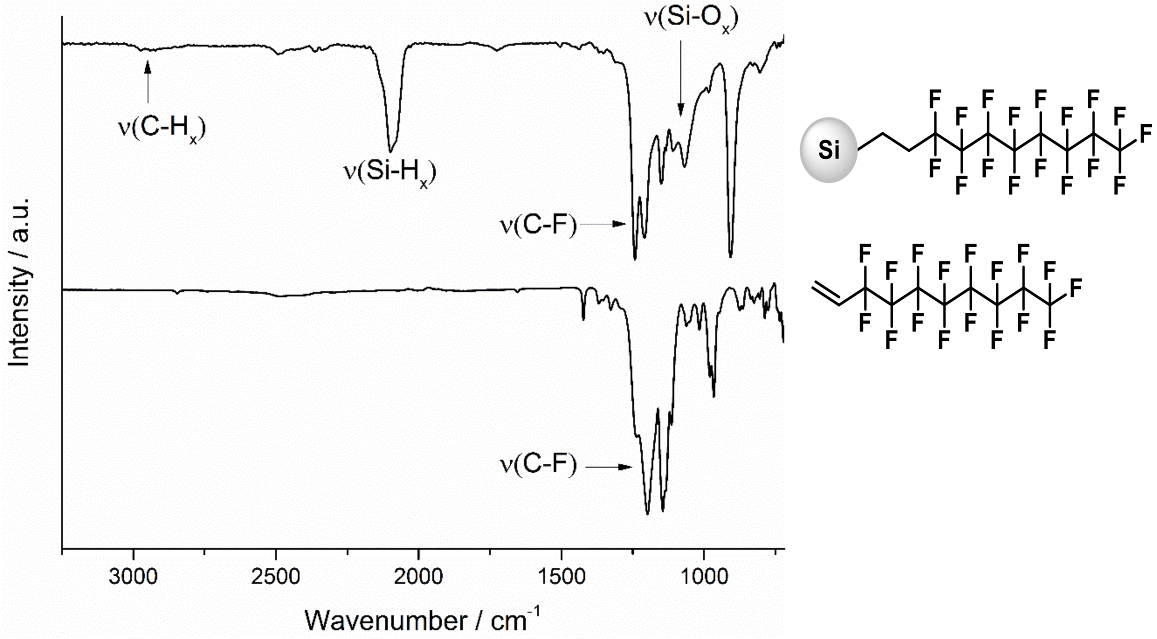


Fig.5-5 FTIR spectra of 1H,1H,2H-perfluoro-1-decene, and 1H,1H,2H-perfluoro-1-decene functionalized SiNCs.

Seebeck Coefficient

Fig.5-6 shows the dependence of the Seebeck coefficient of PEDOT:PSS films on the dopant concentration. Doping with SiNCs/1H,1H,2H-perfluoro-1-decene shows a similar behavior as with SiNCs-ET-1 until a dopant concentration of 12.5 wt%. Concentrations of 15% and higher lead to a significant increase of the Seebeck coefficient with SiNC/1H,1H,2H-perfluoro-1-decene. At a dopant concentration of 40 wt% the Seebeck coefficient has a value of 23 V/K which is 15% higher than the value of neat PEDOT:PSS. Unfortunately, the complex films were destroyed after doping with more than 40 wt% of SiNCs. So the higher performance *p*-type semiconductor complexes need to be investigated.

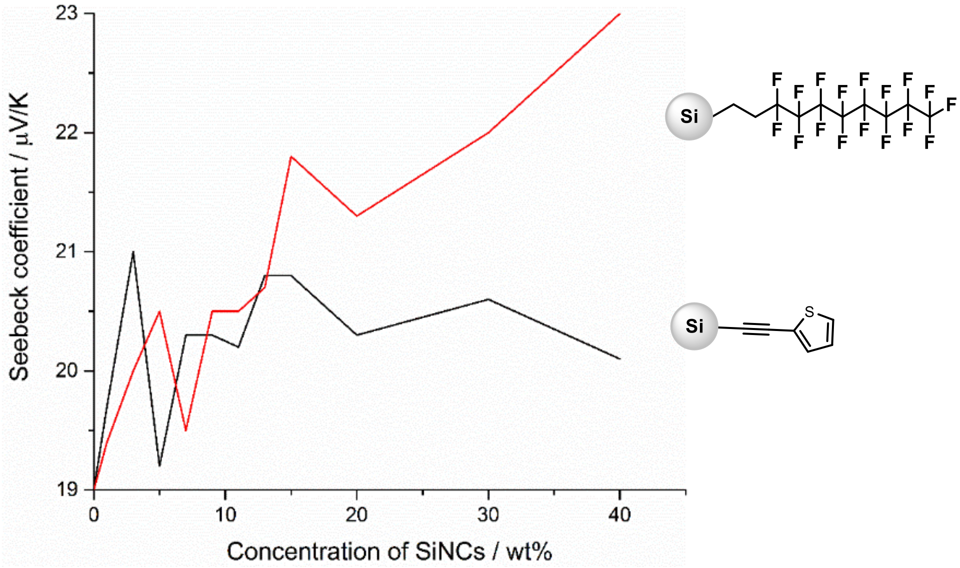


Fig.5-6 The Seebeck coefficient plot of SiNCs/PEDOT:PSS composites: doping with (red) 1H,1H,2H-perfluoro-1-decene, (black) ET-1 functionalized SiNCs

5.3 PEDOT:PSS Materials Doping with B/SiNCs

In order to improve the *p*-type semiconductor character of SiNCs, boron-doped SiNCs were prepared. Therefore, H_3BO_3 (in EtOH) was doped into HSQ (in Toluene) by the following procedure:

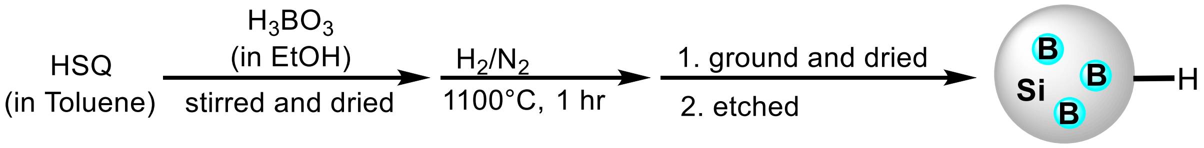


Fig.5-7 Synthesis of B-doped SiNCs.

	A	B	C	D
H_3BO_3	0.5 g	1.0 g	1.5 g	2.0 g
HSQ	5 g	5 g	5 g	5 g

Table.5-1 Different concentrations H_3BO_3 of doped SiNCs

Raman Spectra

From the Raman spectra, the band of silicon can be found around 510 cm^{-1}. In the interval from 580 cm^{-1} to 680 cm^{-1}, the spectra show a broad peak, which is attributed to the boron doped in silicon nanoparticles. Thus, Raman spectroscopy proves the successful doping of SiNCs with boron.

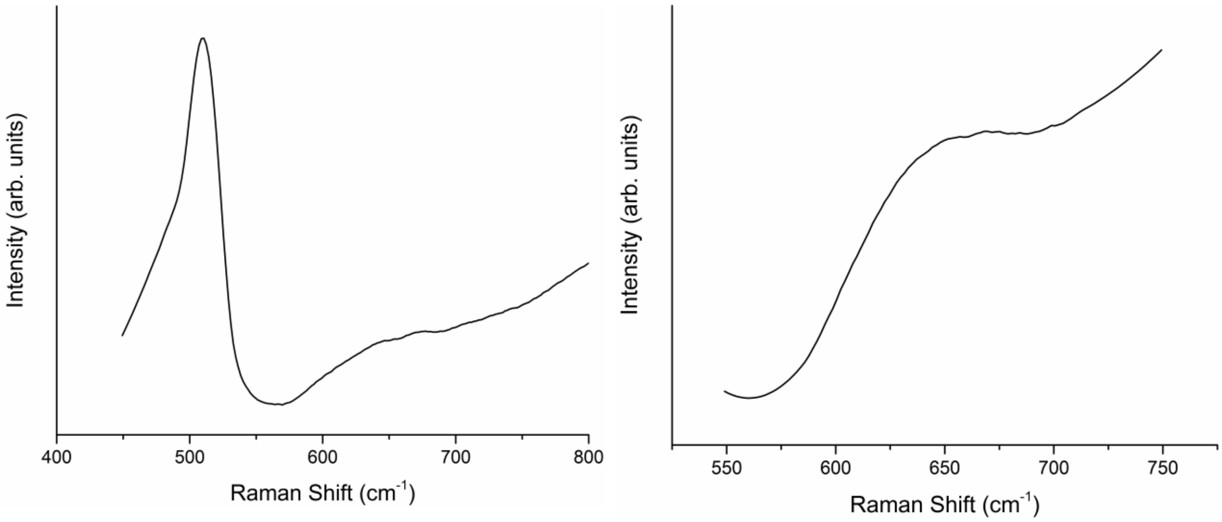


Fig.5-8 (Left) Raman spectra of B/SiNCs; (right) enlargement of the left one.

Seebeck Coefficient

The four samples A, B, C, D (Table. 5-2), and non-doped SiNCs were dispersed in a methanol solution to obtain the concentration of 0.5 mg/mL, 1.0 mg/mL, and 1.5 mg/mL.

	Pure SiNCs	A	B	C	D
0.5 mg/ml	23.8	26.5	29.2	30.6	33.9
1.0 mg/ml	23.9	27.5	30.1	34.0	31.0
1.5 mg/ml	23.7	27.9	30.9	36.0	33.7

Table.5-2 Different Seebeck coefficient value

According to Fig.5-9, the Seebeck coefficient is about 23.9 μV/K for the pure SiNCs/PEDOT:PSS composite. When utilizing B/SiNCs, higher Seebeck coefficients are obtained. The maximum value about 36 μV/K is reached for sample C at a concentration of 1.5 mg/mL, which is an improvement of 51%. More interestingly, for low concentrations of boron doping, the Seebeck coefficient values exhibit an enhancement with increasing B/SiNCs concentration. But samples D (0.5 mg/ml, 1.0 mg/ml, and 1.5 mg/ml) exhibit different Seebeck coefficient values, which was assumed B/SiNCs or B/SiNCs/PEDOT:PSS composite properties change due to too high boron concentration. It is expecting that this needs further investigation.

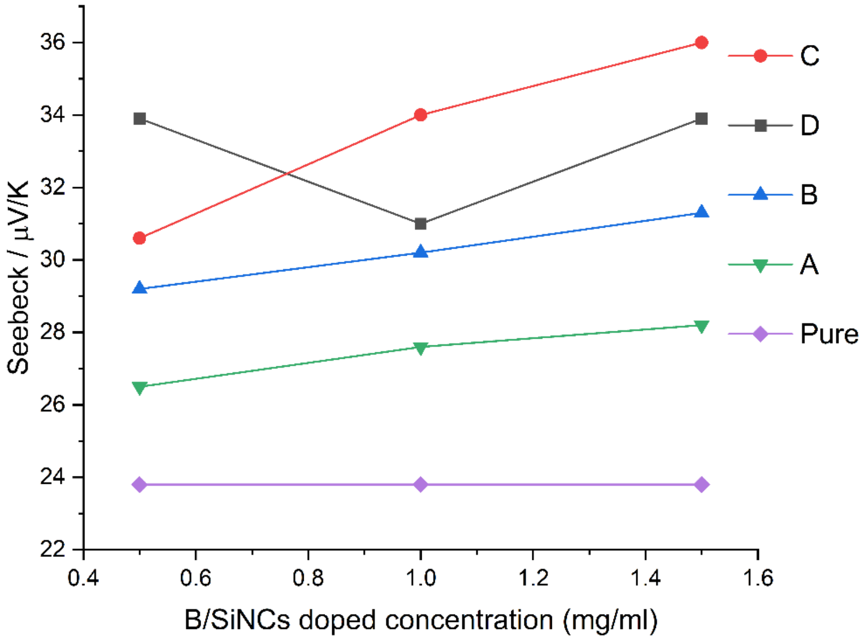


Fig.5-9 The Seebeck coefficient plot of B/SiNCs / PEDOT:PSS composites.

Fourier Transform Infrared Spectra (FTIR)

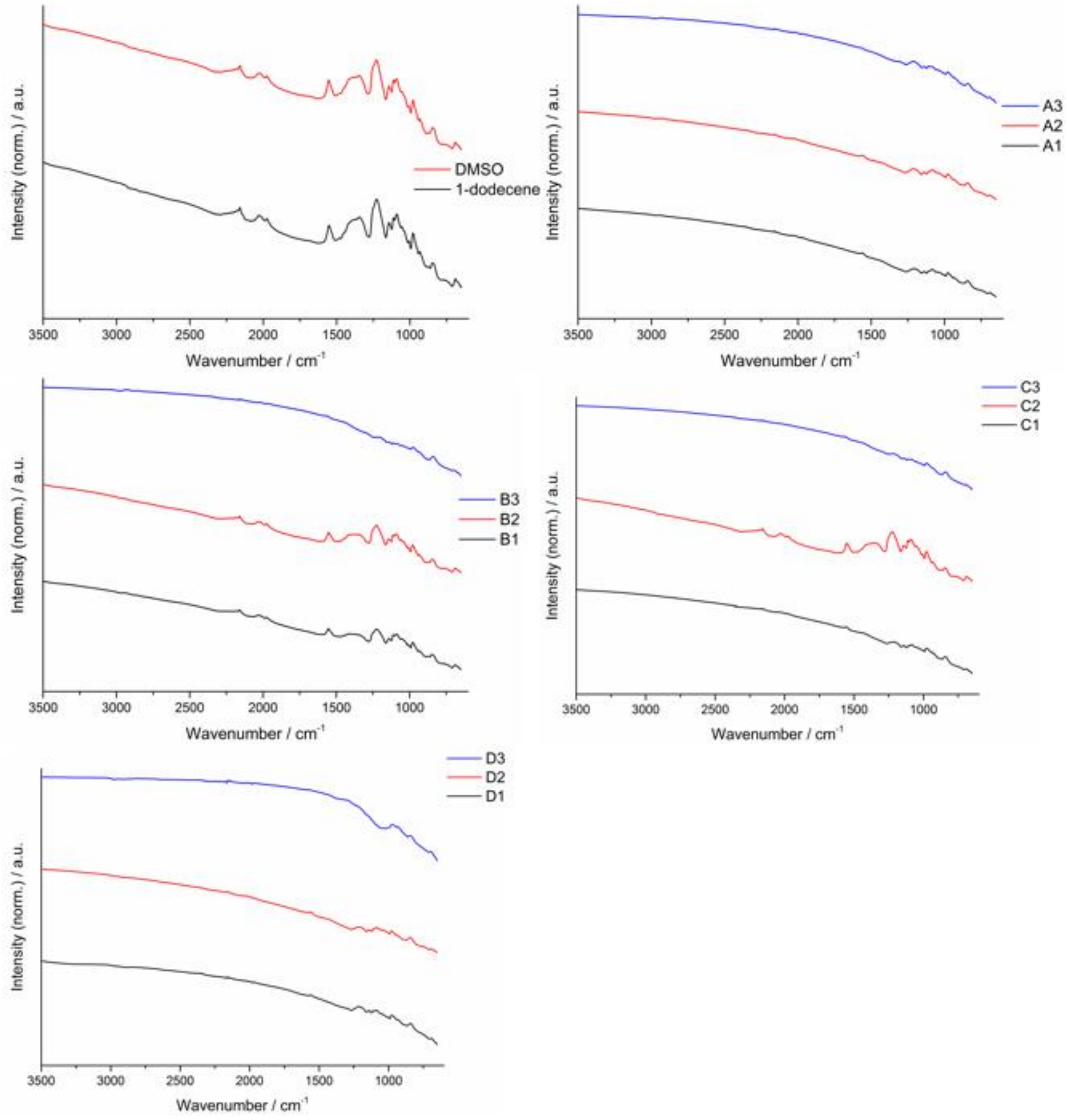


Fig.5-10 FTIR spectra of B/SiNCs/PEDOT:PSS films, B/SiNCs concentration (mg/mL): A1-0.5, A2-1.0, A3-1.5, B1-0.5, B2-1.0, B3-1.5, C1-0.5, C2-1.0, C3-1.5, D1-0.5, D2-.0, D3-1.5.

For the application of conductive polymers, FTIR can be used to determine if the films are changed. Since the films cannot be peeled off from the substrate, FTIR testing becomes very challenging and here we only perform qualitative analysis. From all the above spectra, significant changes are not found, and here it is illustrated that the films are not damaged.

B/SiNCs Surface Functionalization Preliminary Test

1-Dodecene functionalized B/SiNCs was investigated, and as shown in the Fig.5-11 below, 1-dodecene can be successfully modified onto the surface of B/SiNCs.

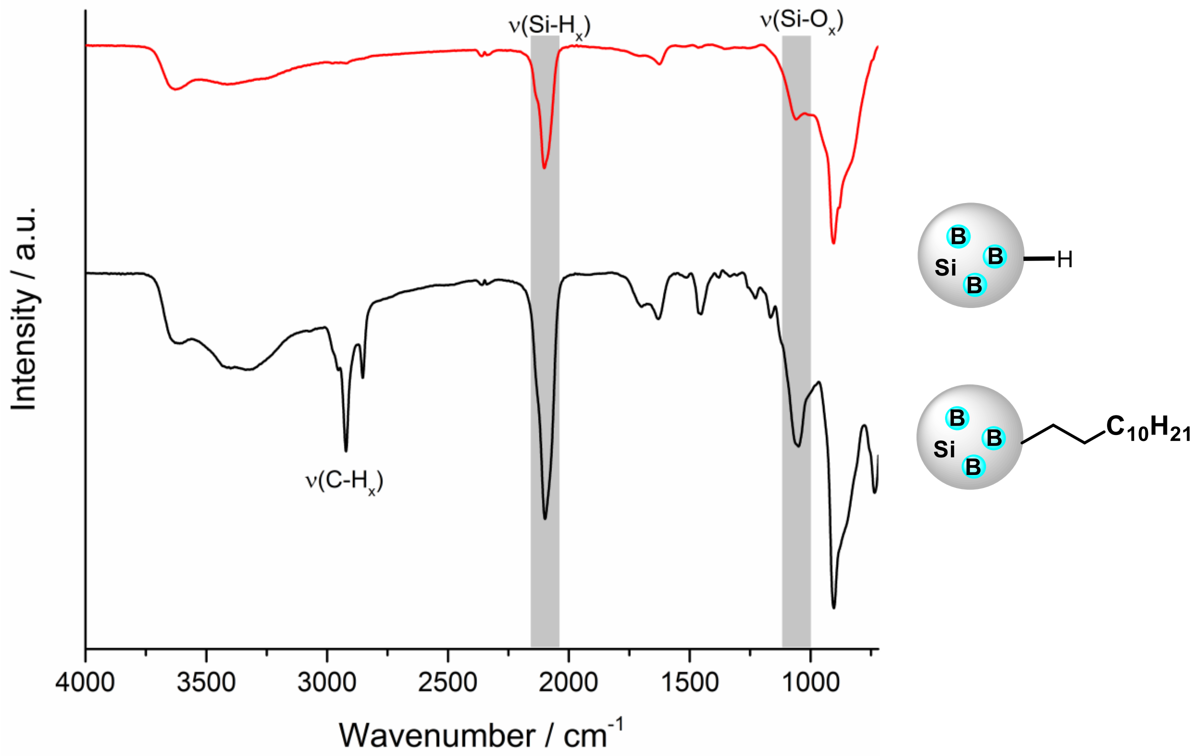


Fig.5-11 FTIR spectra of 1-dodecene functionalized B/SiNCs

5.4 Summary and Conclusion

The two-steps modification method can be applied to a series of conjugated ethynylthiophene systems. After surface functionalization, SiNCs-ET-1 was doped into PEDOT:PSS, there was a significant change in the GIWAXS pattern, proving that SiNCs-ET-1 is favourable for PEDOT:PSS. To get *p*-type semiconductors, perfluorinated nanoparticles were synthesised using microwave method, but the PEDOT:PSS film Seebeck coefficient was not significantly improved.

For the conducting polymer's application of SiNCs, *p*-type semiconductors are currently the optimal solution. B doped SiNCs was obtained with different concentration of B. The Seebeck coefficient values of PEDOT:PSS can be enhanced to a maximum value of about 36 μV/K by doping with B/SiNCs, which offers promise for future applications to improve the conductivety of PEDOT:PSS.

6. Summary and Conclusion

First of all, various series of alkyne-terminated conjugated groups can be obtained by Sonogashira coupling reactions and deprotection reactions. These can be used to enrich the surface group species of nanoparticles. ^{1}H and ^{13}C NMR and FTIR spectra demonstrate the presence of signature functional groups. Organolithium reagents are used to substitute the hydrogen of alkyne-terminated ligands to obtain new conjugated organolithium reagents, which can be modified for the surface functionalization of nanoparticles. Co-functionalization of the SiNCs surface with alkyne-terminated conjugated groups and 1-dodecene is possible via the two-step modification method. The presence of both groups is detected via FTIR spectroscopy. The PL redshift is caused by the grafted ethynylaryl, and 1-dodecene capping prevents oxidation and enhances solubility while optical properties of the SiNCs remain. The surface coverage of the SiNCs decreases with the enlargement of the bulkier surface groups but it still exhibits good photoluminescence performance. TGA elucidates that the SiNCs surface coverage is improved via the second functionalization step. Subsequent studies could proceed to in-gap states of SiNCs modified with large conjugate groups.

SiNCs modified with perfluorinated groups were successfully obtained by microwave reactions. Doping of PEDOT:PSS with these modified SiNCs resulted in slightly higher Seebeck coefficients in comparison to pure PEDOT:PSS complexes. In pursuit of higher Seebeck coefficients, B/SiNCs were synthesized and doped into the conducting polymers. As expected, Raman spectroscopy demonstrated the presence of boron, while the complexes exhibited higher Seebeck coefficients up to about 36 V/K (a 51% growth in comparison to pure PEDOT:PSS), and FTIR spectra proved that the complex films were not disrupted.

In the future, boron doped SiNCs modified with conjugated groups should be explored, including their potential applications in conducting polymers.

7. Experimental Procedures

7.1 Synthesis of Two Different Species Conjugative Systems

General information

Unless noted, all commercial reactants and catalysis were purchased from Sigma-Aldrich used directly without further purification. Dry THF and diethyl ether were obtained from an MBraun SPS 800 solvent purification system. Nuclear magnetic resonance (NMR) spectra were measured on a ARX-300 from Bruker in deuterated chloroform at 300 K. FTIR spectra were measured with a Bruker Vertex 70 FTIR using a Platinum ATR from Bruker. Photoluminescence (PL) spectra were taken with an AVA-Spec 2048 from Avantes using a Prizmatix (LED Current controller) as light source.

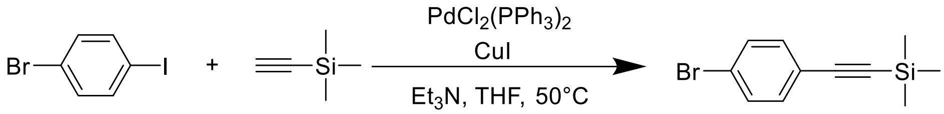
Considering several experimental steps were needed to get the desired products, some reactions were repeated in order to obtain sufficient products.

Phenylacetylene – PE1 (NMR check)

1H NMR (400 MHz, Chloroform-d) δ 7.54 – 7.47 (m, 2H), 7.33 (m, 3H), 3.08 (s, 1H).

13C NMR (101 MHz, Chloroform-d) δ 132.28, 128.93, 128.45, 122.26, 83.80, 77.28.

((4-bromophenyl)ethynyl)trimethylsilane



Reactants *Products*

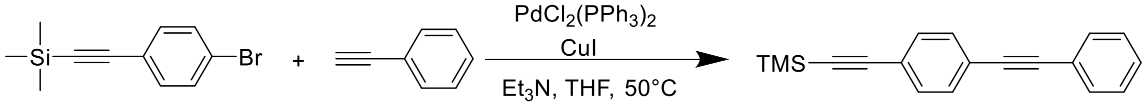
Formula	C_6H_4BrI	$C_5H_{10}Si$	CuI	$C_{36}H_{30}Cl_2P_2Pd$	Formula	$C_{11}H_{13}BrSi$
MW	282.91	98.22	190.45	701.90	MW	253.21
Limiting?	***Yes***	No	No	No	Equivalents	
Equivalents	***1.00***	***1.00***	***0.04***	***0.04***	%Completion	
Sample Mass		294.66mg	22.85mg	84.23mg	Expected Mass	759.64mg
%Weight					Expected Moles	3.00mmol
Molarity					Measured Mass	***565.80mg***
Density		***709.00mg/mL***			Purity	
Volume		415.60mmL			Product Mass	565.80mg
Reactant Moles	***3.00mmol***	3.00mmol	120.00μmol	120.00μmol	Product Moles	2.23mmol
Reactant Mass	848.72mg	294.66mg	22.85mg	84.23mg	%Yield	74.48%

To a Schlenk flask equipped with a stir bar, were added the 1-Bromo-4-iodobenzene (1.0 eq, 3.00 mmol, 848.72 mg), $PdCl_2(PPh_3)_2$ (4%, 0.12 mmol, 84.23 mg), CuI (4%, 0.12 mmol, 22.85 mg), trimethylamine (30 ml), dry THF (30 ml) and ethynyltrimethylsilane (1.0 eq, 3.0 mmol, 0.42 mL) at room temperature under argon. Then the reaction mixture was stirred at 50 °C overnight. The mixture was quenched with saturated NH_4Cl solution and extracted with CH_2Cl_2. The combined organic extracts were washed with water and brine, and dried over anhydrous Na_2SO_4. Then the reaction mixture was purified by flash column chromatography on silica gel to afford the desired ((4-bromophenyl)ethynyl)trimethylsilane.

1H NMR (400 MHz, Chloroform-d) δ 7.43 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 0.24 (s, 9H).

13C NMR (101 MHz, Chloroform-d) δ 133.53, 131.62, 122.89, 122.24, 104.00, 95.73, 0.02.

1-(phenylethynyl)-4-[(trimethylsilyl)ethynyl]benzene



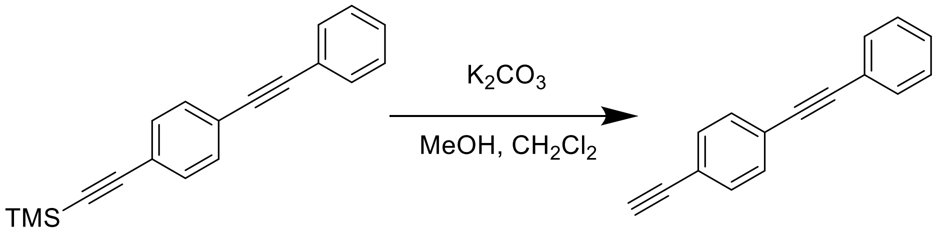
Reactants					*Products*	
Formula	$C_{11}H_{13}BrSi$	C_8H_6	CuI	$C_{36}H_{30}Cl_2P_2Pd$	Formula	$C_{19}H_{18}Si$
MW	253.21	102.14	190.45	701.90	MW	274.44
Limiting?	***Yes***	No	No	No	Equivalents	
Equivalents	***1.00***	***1.20***	***0.04***	***0.04***	%Completion	
Sample Mass		245.13mg	15.24mg	56.15mg	Expected Mass	548.88mg
%Weight					Expected Moles	2.00mmol
Molarity					Measured Mass	***532.50mg***
Density		***930.00mg/mL***			Purity	
Volume		263.58mmL			Product Mass	532.50mg
Reactant Moles	***2.00mmol***	2.40mmol	80.00µmol	80.00µmol	Product Moles	1.94mmol
Reactant Mass	506.43mg	245.13mg	15.24mg	56.15mg	%Yield	97.02%

To a Schlenk flask equipped with a stir bar, were added the ((4-bromophenyl)ethynyl)trimethylsilane (1.0 eq, 2.00 mmol, 506.43 mg), $PdCl_2(PPh_3)_2$ (4%, 0.08 mmol, 56.15 mg), CuI (4%, 0.08 mmol, 15.24 mg), trimethylamine (30 ml), dry THF (30 ml) and phenylacetylene (1.2 eq, 3.40 mmol, 0.27 mL) at room temperature under argon. Then the reaction mixture was stirred at 50 °C overnight. The mixture was quenched with saturated NH_4Cl solution and extracted with CH_2Cl_2. The combined organic extracts were washed with water and brine, and dried over anhydrous Na_2SO_4. Then the reaction mixture was purified by flash column chromatography on silica gel to afford the desired 1-(phenylethynyl)-4-[(trimethylsilyl)ethynyl]benzene.

1H NMR (400 MHz, Chloroform-d) δ 7.52 (dd, J = 6.6, 2.9 Hz, 2H), 7.45 (m, 4H), 7.34 (m, 3H), 0.26 (s, 9H).

13C NMR (101 MHz, Chloroform-d) δ 132.04, 131.77, 131.53, 128.63, 128.54, 123.49, 123.15, 123.05, 104.82, 96.41, 91.43, 89.17, 0.07.

1-ethynyl-4-(phenylethynyl)benzene – PE2



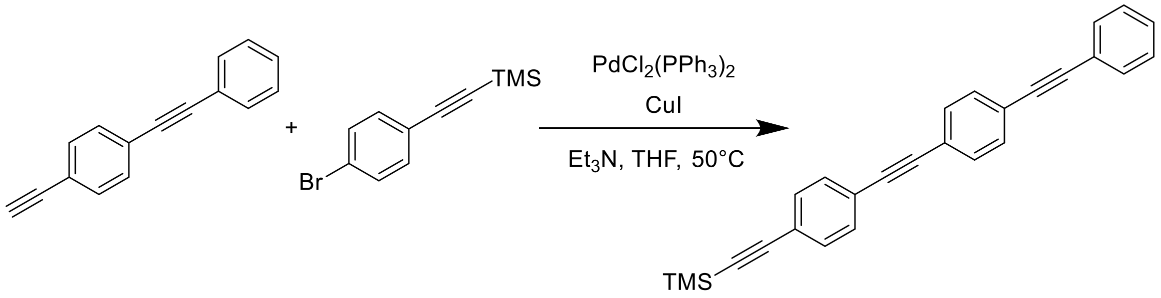
Reactants			*Products*	
Formula	$C_{19}H_{18}Si$	CK_2O_3	Formula	$C_{16}H_{10}$
MW	274.44	138.20	MW	202.26
Limiting?	***Yes***	No	Equivalents	
Equivalents	***1.00***	***2.00***	%Completion	
Sample Mass		1.34g	Expected Mass	977.24mg
%Weight			Expected Moles	4.83mmol
Molarity			Measured Mass	***932.40mg***
Density			Purity	
Volume			Product Mass	932.40mg
Reactant Moles	4.83mmol	9.66mmol	Product Moles	4.61mmol
Reactant Mass	***1.33g***	1.34g	%Yield	95.41%

To a flask equipped with a stir bar, were added the above product 1-(phenylethynyl)-4-[(trimethylsilyl)ethynyl]benzene (1.0 eq, 4.83 mmol, 1.33 g) in methanol (20 mL) and DCM (20 mL). Potassium carbonate (2.0 eq, 9.66 mmol, 1.34 g) was added. The reaction was stirred at room temperature overnight. The reaction was poured into water, and the aqueous layer was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$, and the solvent was removed to afford the desired 1-ethynyl-4-(phenylethynyl)benzene.

1H NMR (400 MHz, Chloroform-d) δ 7.53 (dd, J = 6.7, 3.0 Hz, 2H), 7.48 (m, 4H), 7.35 (t, J = 3.2 Hz, 3H), 3.17 (s, 1H).

13C NMR (101 MHz, Chloroform-d) δ 132.22, 131.80, 131.63, 128.69, 128.55, 123.94, 88.97, 83.42, 79.02.

trimethyl[4-(4-(phenylethynyl)phenylethynyl)phenylethynyl]silane



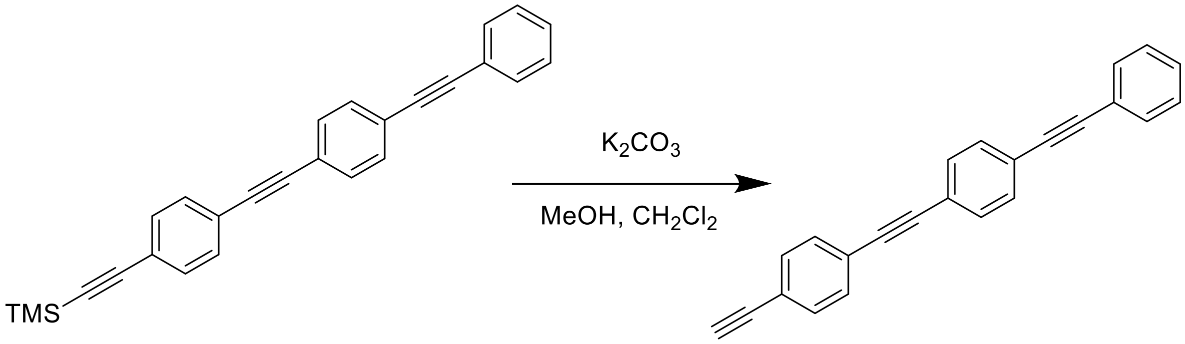
Reactants					*Products*	
Formula	$C_{16}H_{10}$	$C_{11}H_{13}BrSi$	CuI	$C_{36}H_{30}Cl_2P_2Pd$	Formula	$C_{27}H_{22}Si$
MW	202.26	253.21	190.45	701.90	MW	374.56
Limiting?	***Yes***	No	No	No	Equivalents	
Equivalents	***1.00***	***1.00***	***0.04***	***0.04***	%Completion	
Sample Mass		2.53g	76.18mg	280.76mg	Expected Mass	3.75g
%Weight					Expected Moles	10.00mmol
Molarity					Measured Mass	***2.14g***
Density					Purity	
Volume					Product Mass	2.14g
Reactant Moles	***10.00mmol***	10.00mmol	400.00µmol	400.00µmol	Product Moles	5.71mmol
Reactant Mass	2.02g	2.53g	76.18mg	280.76mg	%Yield	57.13%

To a Schlenk flask equipped with a stir bar, were added the 1-ethynyl-4-(phenylethynyl)benzene (1.0 eq, 10.00 mmol, 2.02 g), $PdCl_2(PPh_3)_2$ (4%, 0.40 mmol, 280.76 mg), CuI (4%, 0.4 mmol, 76.18 mg), trimethylamine (100 ml), dry THF (100 ml) and 1-bromo-4-(trimethylsilylethynyl)benzene (1.0 eq, 10.00 mmol, 2.53 g) at room temperature under argon. Then the reaction mixture was stirred at 50 °C overnight. The mixture was quenched with saturated NH_4Cl solution and extracted with CH_2Cl_2. The combined organic extracts were washed with water and brine, and dried over anhydrous Na_2SO_4. Then the reaction mixture was purified by flash column chromatography on silica gel to afford the desired trimethyl[4-(4-(phenylethynyl)phenylethynyl)phenylethynyl]silane.

1H NMR (400 MHz, Chloroform-d) δ 7.54 (dd, J = 6.7, 2.9 Hz, 2H), 7.50 (m, 4H), 7.46 (m, 4H), 7.36 (m, 3H), 0.26 (s, 9H).

13C NMR (101 MHz, Chloroform-d) δ 132.09, 131.79, 131.72, 131.70, 131.56, 128.55, 123.50, 122.94, 121.08, 89.15, 88.15, 0.07.

4-(2-(4-ethynylphenyl)-ethynyl)-1-(2-phenylethynyl)benzene - PE 3



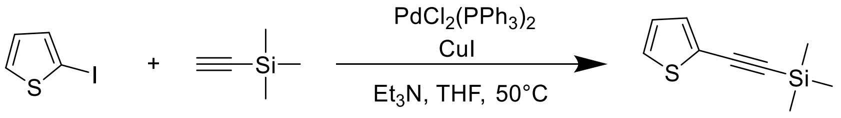
Reactants			*Products*	
Formula	$C_{27}H_{22}Si$	CK_2O_3	Formula	$C_{24}H_{14}$
MW	374.56	138.20	MW	302.38
Limiting?	***Yes***	No	Equivalents	
Equivalents	***1.00***	***2.00***	%Completion	
Sample Mass		789.62mg	Expected Mass	863.80mg
%Weight			Expected Moles	2.86mmol
Molarity			Measured Mass	***785.00mg***
Density			Purity	
Volume			Product Mass	785.00mg
Reactant Moles	2.86***mmol***	5.71mmol	Product Moles	2.60mmol
Reactant Mass	***1.07g***	789.62mg	%Yield	90.88%

To a flask equipped with a stir bar, were added the above product trimethyl[4-(4-(phenylethynyl)phenylethynyl)phenylethynyl]silane (1.0 eq, 15.0 mmol) in methanol (40 mL) and CH_2Cl_2 (40 mL). Potassium carbonate (2.0 eq, 30.0 mmol, 4.15 g) was added. The reaction was stirred at room temperature overnight. The reaction was poured into water, and the aqueous layer was extracted with CH_2Cl_2. The organic layer was dried over magnesium sulfate, and the solvent was removed by distillation to afford the desired 4-(2-(4-ethynylphenyl)-ethynyl)-1-(2-phenylethynyl)benzene.

1H NMR (400 MHz, Chloroform-d) δ 7.54 (dd, J = 6.6, 3.0 Hz, 2H), 7.51 (m, 4H), 7.48 (m, 4H), 7.36 (dd, J = 5.0, 2.0 Hz, 3H), 3.18 (s, 1H).

13C NMR (101 MHz, Chloroform-d) δ 132.26, 131.80, 131.73, 131.64, 128.56, 123.58, 123.14, 122.86, 122.24, 83.40, 79.18.

2-[(Trimethylsilyl)ethynyl]thiophene



Reactants *Products*

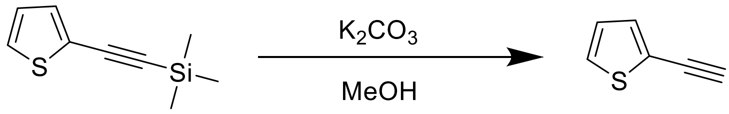
Formula	C_4H_3IS	$C_5H_{10}Si$	CuI	$C_{36}H_{30}Cl_2P_2Pd$	Formula	$C_9H_{12}SSi$
MW	210.03	98.22	190.45	701.90	MW	180.34
Limiting?	***Yes***	No	No	No	Equivalents	
Equivalents	***1.00***	***1.30***	***0.04***	***0.04***	%Completion	
Sample Mass	4.20g	2.55g	152.36mg	561.52mg	Expected Mass	3.61g
%Weight					Expected Moles	20.00mmol
Molarity					Measured Mass	***3.47g***
Density	***1.90g/mL***	***709.00mg/mL***			Purity	
Volume	2.21mL	3.60mL			Product Mass	3.47g
Reactant Moles	***20.00mmol***	26.00mmol	800.00µmol	800.00µmol	Product Moles	19.24mmol
Reactant Mass	4.20g	2.55g	152.36mg	561.52mg	%Yield	96.21%

To a Schlenk flask equipped with a stir bar, were added the 2-Iod-thiophen (1.0 eq, 20.00 mmol, 2.21 mL), $PdCl_2(PPh_3)_2$ (4%, 0.80 mmol, 561.52 mg), CuI (0.80 mmol, 152.36 mg), ethynyltrimethylsilane (1.3 eq, 26.0 mmol, 3.60 mL), trimethylamine (60 ml) and dry THF (60 ml) at room temperature under argon. Then the reaction mixture was stirred at 50 °C overnight. The mixture was quenched with saturated NH_4Cl solution and extracted with CH_2Cl_2. The combined organic extracts were washed with water and brine, and dried over anhydrous Na_2SO_4. Then the reaction mixture was purified by flash column chromatography on silica gel to afford the desired 2-[(Trimethylsilyl)ethynyl]thiophene.

1H NMR (400 MHz, Chloroform-d) δ 7.23 (d, J = 4.4 Hz, 1H), 6.95 (t, J = 4.4 Hz, 1H), 0.25 (s, 9H).

13C NMR (101 MHz, Chloroform-d) δ 132.76, 127.41, 126.98, 123.37, 98.86, 97.66, 0.01.

2-ethynylthiophene – ET1



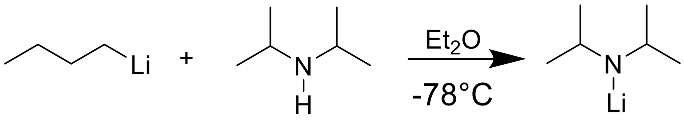
Reactants			*Products*	
Formula	$C_9H_{12}SSi$	CK_2O_3	Formula	C_6H_4S
MW	180.34	138.20	MW	108.16
Limiting?	***Yes***	No	Equivalents	
Equivalents	***1.00***	***2.00***	%Completion	
Sample Mass		18.80g	Expected Mass	7.35g
%Weight			Expected Moles	68.00mmol
Molarity			Measured Mass	***7.24g***
Density			Purity	
Volume			Product Mass	7.24g
Reactant Moles	***68.00mmol***	136.00mmol	Product Moles	66.94mmol
Reactant Mass	12.26g	18.80g	%Yield	98.44%

To a Schlenk flask equipped with a stir bar, were added the above product 2-[(Trimethylsilyl)ethynyl]thiophene (1.0 eq, 68.00 mmol, 12.26 g) in methanol (60 mL). Potassium carbonate (2.0 eq, 136.00 mmol, 18.8 g) was added. The reaction was stirred at room temperature for 30 mins. The reaction was poured into water, and the aqueous layer was extracted with ether. The organic layer was dried over MgSO4, and the solvent was removed by rotary evaporator. The product was distilled with a short path condenser to afford the 2-ethynylthiophene as a clear yellow oil.

1H NMR (400 MHz, Chloroform-d) δ 7.31 – 7.26 (m, 2H), 6.98 (dd, J = 5.2, 3.6 Hz, 1H), 3.34 (s, 1H).

13C NMR (101 MHz, Chloroform-d) δ 133.21, 127.65, 127.02, 122.17, 81.35, 77.09.

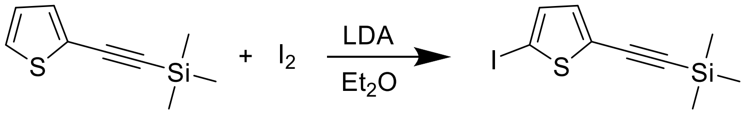
LDA



Reactants			Products	
Formula	C_4H_9Li	$C_6H_{15}N$	Formula	$C_6H_{14}LiN$
MW	64.06	101.19	MW	107.13
Limiting?	***Yes***	No	Equivalents	
Equivalents	***0.92***	***1.00***	%Completion	
Sample Mass	1.99g	3.42g	Expected Mass	3.61g
%Weight			Expected Moles	33.70mmol
Molarity	***2.50M***		Measured Mass	
Density		***722.00mg/mL***	Purity	
Volume	12.40mL	4.74mL	Product Mass	
Reactant Moles	***31.00mmol***	***33.80mmol***	Product Moles	
Reactant Mass	1.99g	3.42g	%Yield	

To a Schlenk flask equipped with a stir bar, a solution of diisopropylamine (3.42 g, 4.74 mL, 33.8 mmol) in diethyl ether (20mL) was cooled at -78°C. n-butyllithium (31.0 mmol, 12.40 mL, 2.5M in hexane) was added dropwise. Then the reaction was stirred at -78°C for 15 min. The mixture was warmed to 0°C for 30 min and then re-cooled to -78°C.

((5-iodothiophen-2-yl)ethynyl)trimethylsilane



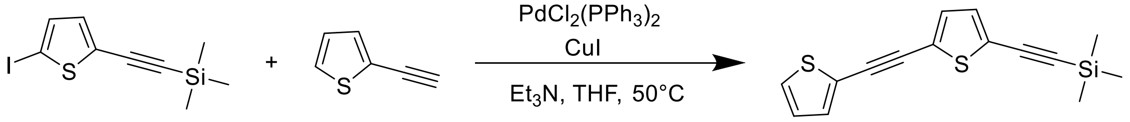
Reactants			*Products*	
Formula	$C_9H_{12}SSi$	I_2	Formula	$C_9H_{11}ISSi$
MW	180.34	253.81	MW	306.24
Limiting?	***Yes***	No	Equivalents	
Equivalents	***1.00***	2.18	%Completion	
Sample Mass	2.80g	8.58g	Expected Mass	4.75g
%Weight			Expected Moles	15.50mmol
Molarity			Measured Mass	***2.99g***
Density	***1.09g/mL***		Purity	
Volume	2.56mL		Product Mass	2.99g
Reactant Moles	***15.50mmol***	***33.80mmol***	Product Moles	9.76mmol
Reactant Mass	2.80g	8.58g	%Yield	62.99%

Trimethyl(thiophen-2-ylethynyl)silane (15.50 mmol, 2.8 g) in diethyl ether (10 mL) at room temperature was then added dropwise to the above LDA solution, and the solution was warmed from -78°C to 0°C for 15 min. After re-cooling to -78°C, iodine (33.80 mmol, 8.6 g) in diethyl ether (60 mL) was added via cannula, and the solution was then warmed to room temperature and stirred overnight. The mixture was quenched with water, and the aqueous layer was extracted with diethyl ether. The combined organic layer was washed with brine and aqueous sodium thiosulfate, and then dried over $MgSO_4$. The solvent was removed under vacuum, and the crude product was purified by silica column chromatography eluting with petroleum ether to afford compound ((5-iodothiophen-2-yl)ethynyl)trimethylsilane as a yellow liquid.

1H NMR (400 MHz, Chloroform-d) δ 7.09 (d, J = 3.8 Hz, 1H), 6.87 (d, J = 3.8 Hz, 1H), 0.24 (s, 9H).

13C NMR (101 MHz, Chloroform-d) δ 136.98, 133.96, 129.61, 101.10, 96.29, 74.89, -0.08.

1-(thiophenethynyl)-4-((trimethylsilyl)ethynyl)thiophene



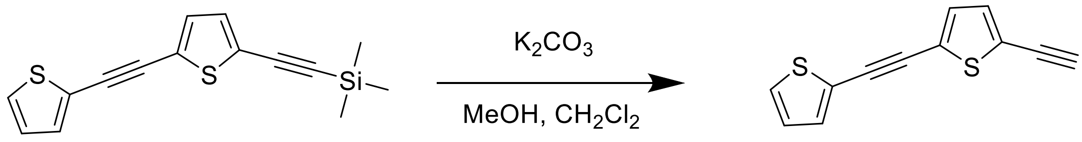
Reactants					*Products*	
Formula	$C_9H_{11}ISSi$	C_6H_4S	CuI	$C_{36}H_{30}Cl_2P_2Pd$	Formula	$C_{15}H_{14}S_2Si$
MW	306.24	108.16	190.45	701.90	MW	286.48
Limiting?	***Yes***	No	No	No	Equivalents	
Equivalents	***1.00***	***1.20***	***0.04***	***0.04***	%Completion	
Sample Mass	1.53g	648.95mg	38.09mg	140.38mg	Expected Mass	1.43g
%Weight					Expected Moles	5.00mmol
Molarity					Measured Mass	***1.33g***
Density	***1.52g/mL***	***1.14g/mL***			Purity	
Volume	1.01mL	569.25mmL			Product Mass	1.33g
Reactant Moles	***5.00mmol***	6.00mmol	200.00μmol	200.00μmol	Product Moles	4.64mmol
Reactant Mass	1.53g	648.95mg	38.09mg	140.38mg	%Yield	92.85%

To a Schlenk flask equipped with a stir bar, were added the ((5-iodothiophen-2-yl)ethynyl)trimethylsilane (1.0 eq, 5.00 mmol, 1.01 mL), $PdCl_2(PPh_3)_2$ (4%, 0.20 mmol, 140.38 mg), CuI (4%, 0.20 mmol, 38.09 mg), trimethylamine (30 ml), dry THF (30 ml) and 2-ethynylthiophene (1.2 eq, 6.00 mmol, 0.57 mL) at room temperature under argon. Then the reaction mixture was stirred at 50 °C overnight. The mixture was quenched with saturated NH_4Cl solution and extracted with CH_2Cl_2. The combined organic extracts were washed with water and brine, and dried over anhydrous Na_2SO_4. Then the reaction mixture was purified by flash column chromatography on silica gel to afford the desired 1-(thiophenethynyl)-4-((trimethylsilyl)ethynyl)thiophene.

1H NMR (400 MHz, Chloroform-d) δ 7.32 (d, J = 5.1 Hz, 1H), 7.29 (d, J = 3.7 Hz, 1H), 7.13 – 7.06 (m, 2H), 7.05 – 6.97 (m, 1H), 0.26 (s, 9H).

13C NMR (101 MHz, Chloroform-d) δ 132.71, 132.65, 131.87, 128.16, 127.37, 124.98, 124.34, 122.67, 100.53, 97.00, 87.18, 85.96, -0.06.

1-(thiophenethynyl)-4-ethynylthiophene - ET2



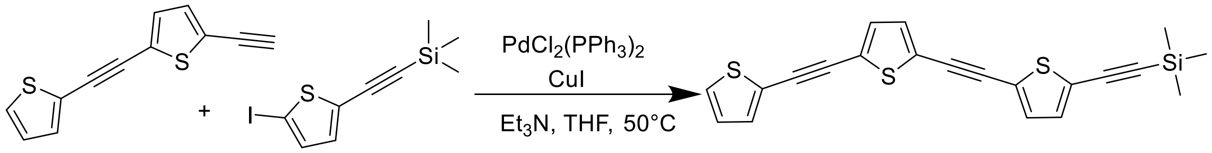
Reactants			*Products*	
Formula	$C_{15}H_{14}S_2Si$	CK_2O_3	Formula	$C_{12}H_6S_2$
MW	286.48	138.20	MW	214.30
Limiting?	***Yes***	No	Equivalents	
Equivalents	***1.00***	***2.00***	%Completion	
Sample Mass		4.18g	Expected Mass	3.24g
%Weight			Expected Moles	15.11 mmol
Molarity			Measured Mass	***3.17g***
Density			Purity	
Volume			Product Mass	3.17g
Reactant Moles	15.11 mmol	30.23mmol	Product Moles	14.79mmol
Reactant Mass	***4.33g***	4.18g	%Yield	97.87%

To the above product 1-(thiophenethynyl)-4-((trimethylsilyl)ethynyl)thiophene (1.0 eq, 15.11 mmol, 4.33 g) in methanol (40 mL) and DCM (40 mL)was added potassium carbonate (4.0 eq, 60.46 mmol, 8.36 g). The reaction was stirred at room temperature overnight. The reaction was poured into water, and the aqueous layer was extracted with DCM. The organic layer was dried over magnesium sulfate, and the solvent was removed to afford the desired 1-(thiophenethynyl)-4-ethynylthiophene.

1H NMR (400 MHz, Chloroform-d) δ 7.33 (d, J = 5.1 Hz, 1H), 7.30 (d, J = 2.6 Hz, 1H), 7.16 (d, J = 3.9 Hz, 1H), 7.11 (d, J = 3.8 Hz, 1H), 7.02 (dd, J = 5.1, 3.7 Hz, 1H), 3.39 (s, 1H).

13C NMR (101 MHz, Chloroform-d) δ 133.16, 132.72, 131.76, 128.25, 127.39, 124.78, 123.67, 122.55, 87.30, 85.72, 82.52, 76.58.

trimethyl((5-((5-(thiophen-2-ylethynyl)thiophen-2-yl)ethynyl)thiophen-2-yl)ethynyl)silane



Reactants

Products

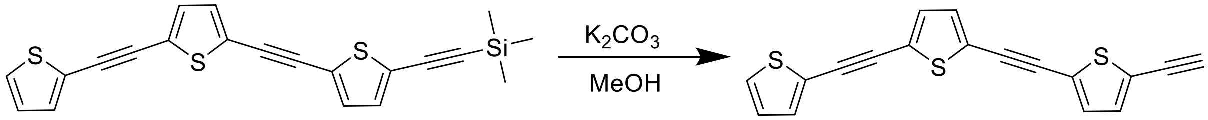
Formula	$C_{12}H_6S_2$	$C_9H_{11}ISSi$	CuI	$C_{36}H_{30}Cl_2P_2Pd$	Formula	$C_{21}H_{16}S_3Si$
MW	214.30	306.24	190.45	701.90	MW	392.62
Limiting?	***Yes***	No	No	No	Equivalents	
Equivalents	***1.00***	***1.50***	***0.04***	***0.04***	%Completion	
Sample Mass		918.71mg	15.24mg	56.15mg	Expected Mass	785.25mg
%Weight					Expected Moles	2.00mmol
Molarity					Measured Mass	***502.60mg***
Density					Purity	
Volume					Product Mass	502.60mg
Reactant Moles	***2.00mmol***	3.00mmol	80.00μmol	80.00μmol	Product Moles	1.28mmol
Reactant Mass	428.60mg	918.71mg	15.24mg	56.15mg	%Yield	64.01%

To a Schlenk flask equipped with a stir bar, were added the ((5-iodothiophen-2-yl)ethynyl)trimethylsilane (1.50 eq, 3.00 mmol, 918.71 mg), $PdCl_2(PPh_3)_2$ (4%, 0.08 mmol, 56.15 mg), CuI (4%, 0.08 mmol, 15.24 mg), trimethylamine (20 ml) and dry THF (20 ml), 2-ethynyl-5-(thiophen-2-ylethynyl)thiophene (1.00 eq, 0.2 mmol, 428.60 mg) at room temperature under argon. Then the reaction mixture was stirred at 50 °C overnight. The mixture was quenched with saturated NH_4Cl solution and extracted with CH_2Cl_2. The combined organic extracts were washed with water and brine, and dried over anhydrous Na_2SO_4. Then the reaction mixture was purified by flash column chromatography on silica gel to afford the desired trimethyl((5-((5-(thiophen-2-ylethynyl)thiophen-2-yl)ethynyl)thiophen-2-yl)ethynyl)silane.

1H NMR (400 MHz, Chloroform-d) δ 7.33 (d, J = 5.1 Hz, 1H), 7.31 (d, J = 2.4 Hz, 1H), 7.15 (m, J = 3.3 Hz, 2H), 7.11 (s, 2H), 7.03 (dd, J = 5.2, 3.7 Hz, 1H), 0.26 (s, 9H).

13C NMR (101 MHz, Chloroform-d) δ 132.76, 132.52, 132.27, 132.16, 128.28, 127.42, 125.46, 124.22, 123.96, 123.87, 122.60, 87.20, 86.80, 85.88, 84.87.

2-ethynyl-5-((5-(thiophen-2-ylethynyl)thiophen-2-yl)ethynyl)thiophene – ET3



Reactants			*Products*	
Formula	$C_{21}H_{16}S_3Si$	CK_2O_3	Formula	$C_{18}H_8S_3$
MW	392.62	138.20	MW	320.44
Limiting?	***Yes***	No	Equivalents	
Equivalents	***1.00***	***2.00***	%Completion	
Sample Mass		1.20g	Expected Mass	1.39g
%Weight			Expected Moles	4.33mmol
Molarity			Measured Mass	***1.12g***
Density			Purity	
Volume			Product Mass	1.12g
Reactant Moles	4.33***mmol***	8.66mmol	Product Moles	3.50mmol
Reactant Mass	***1.70g***	1.20g	%Yield	80.72%

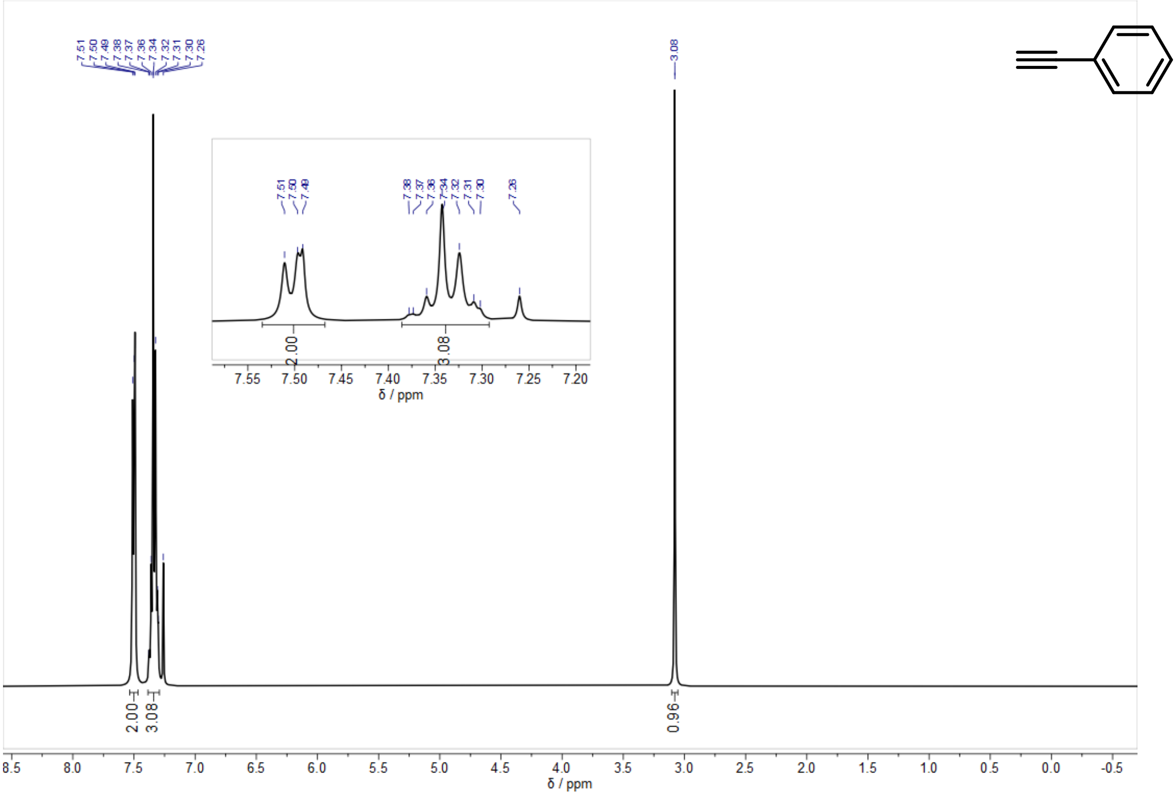
To the above product trimethyl((5-((5-(thiophen-2-ylethynyl)thiophen-2-yl)ethynyl)thiophen-2-yl)ethynyl)silane (1.0 eq, 4.33 mmol, 1.70 g) in methanol (30 mL) and CH_2Cl_2 (30 mL)was added potassium carbonate (2.0 eq, 8.66 mmol, 1.20 g). The reaction was stirred at room temperature overnight. The reaction was poured into water, and the aqueous layer was extracted with CH_2Cl_2. The organic layer was dried over magnesium sulfate, and the solvent was removed by distillation to afford the desired 2-ethynyl-5-((5-(thiophen-2-ylethynyl)thiophen-2-yl)ethynyl)thiophene.

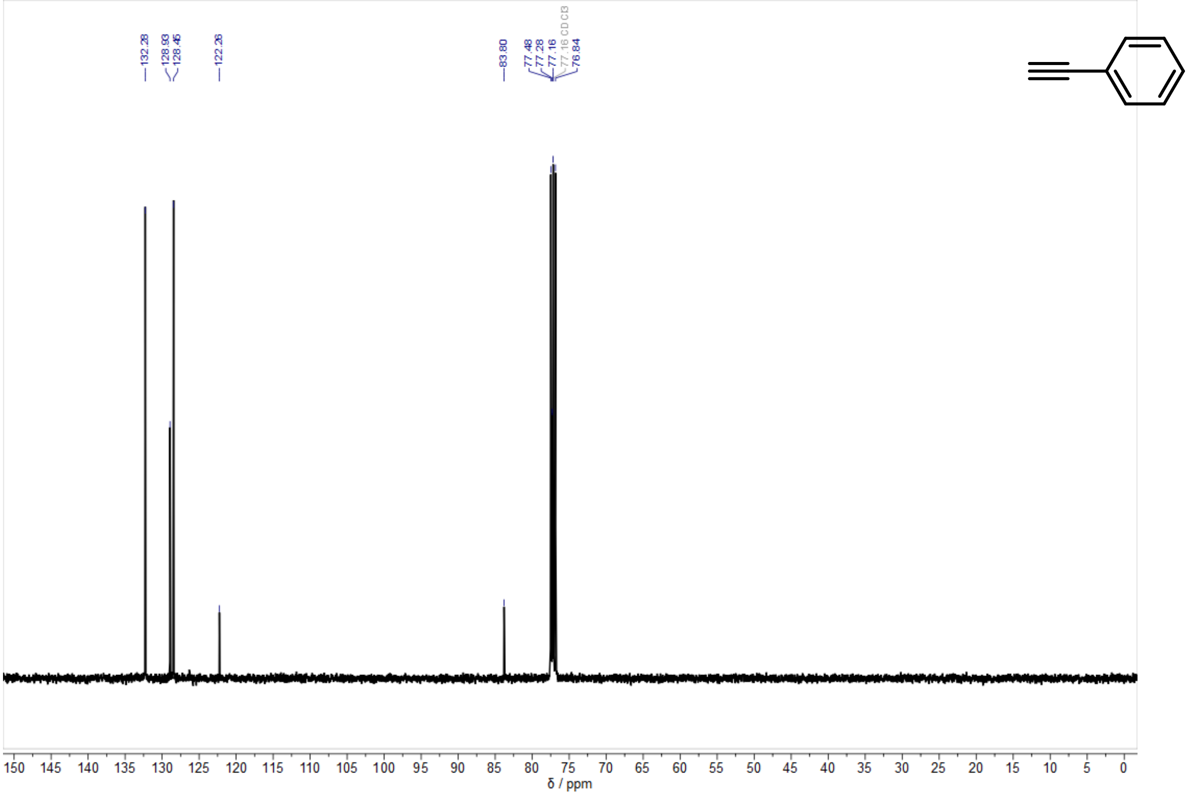
1H NMR (400 MHz, Chloroform-d) δ 7.34 (d, J = 5.1 Hz, 1H), 7.31 (d, J = 3.6 Hz, 1H), 7.15 (dd, J = 10.5, 3.5 Hz, 4H), 7.03 (t, J = 4.4 Hz, 1H), 3.40 (s, 1H).

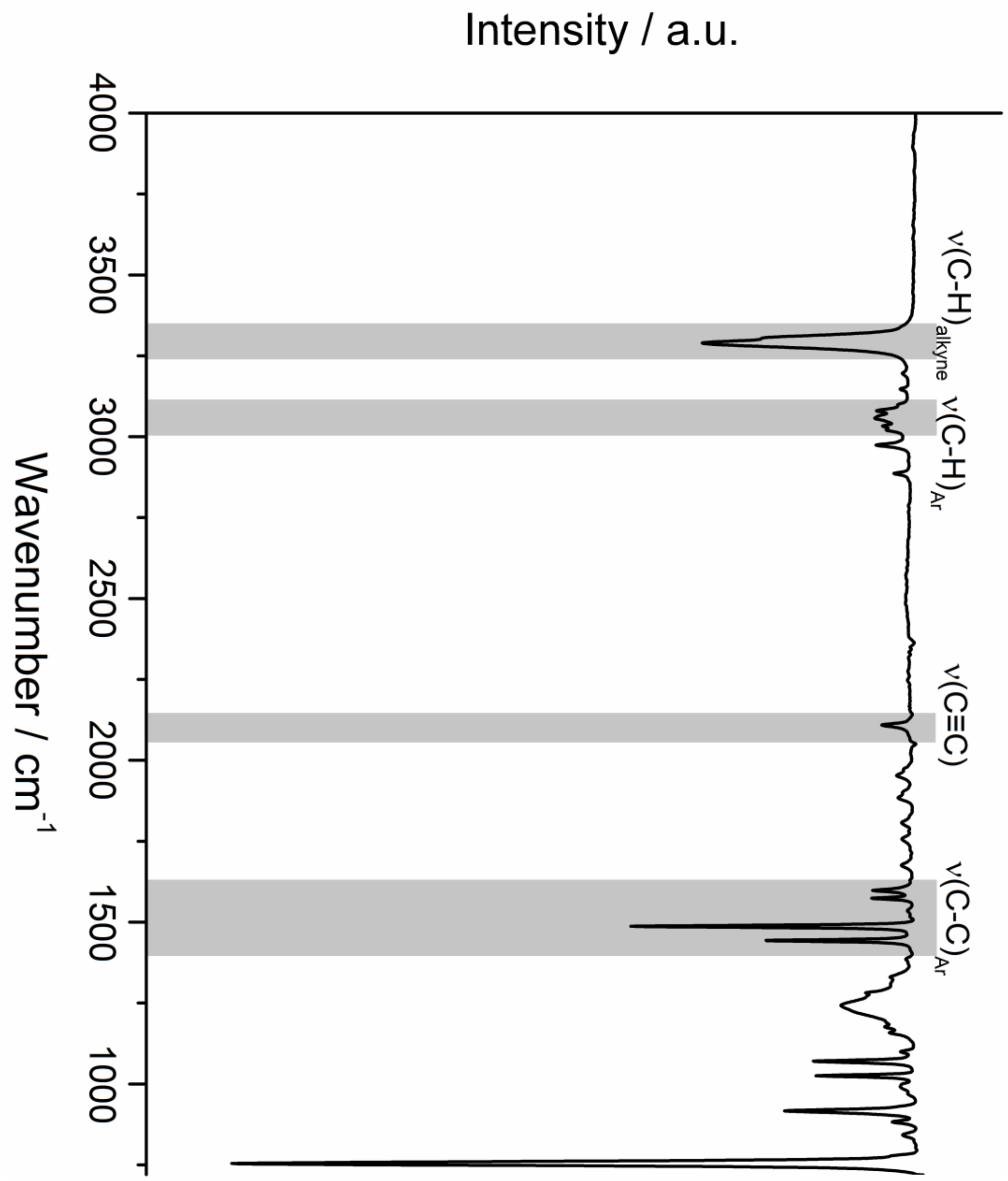
13C NMR (101 MHz, Chloroform-d) δ 133.20, 132.74, 132.60, 132.15, 128.29, 127.41, 125.20, 124.33, 124.10, 124.07, 122.57, 87.91, 86.95, 86.87, 85.85, 82.77, 76.49.

7.2 ^{1}H, ^{13}C NMR and FTIR Spectroscopy

Phenylacetylene 1



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Wavenumber / cm^{-1}
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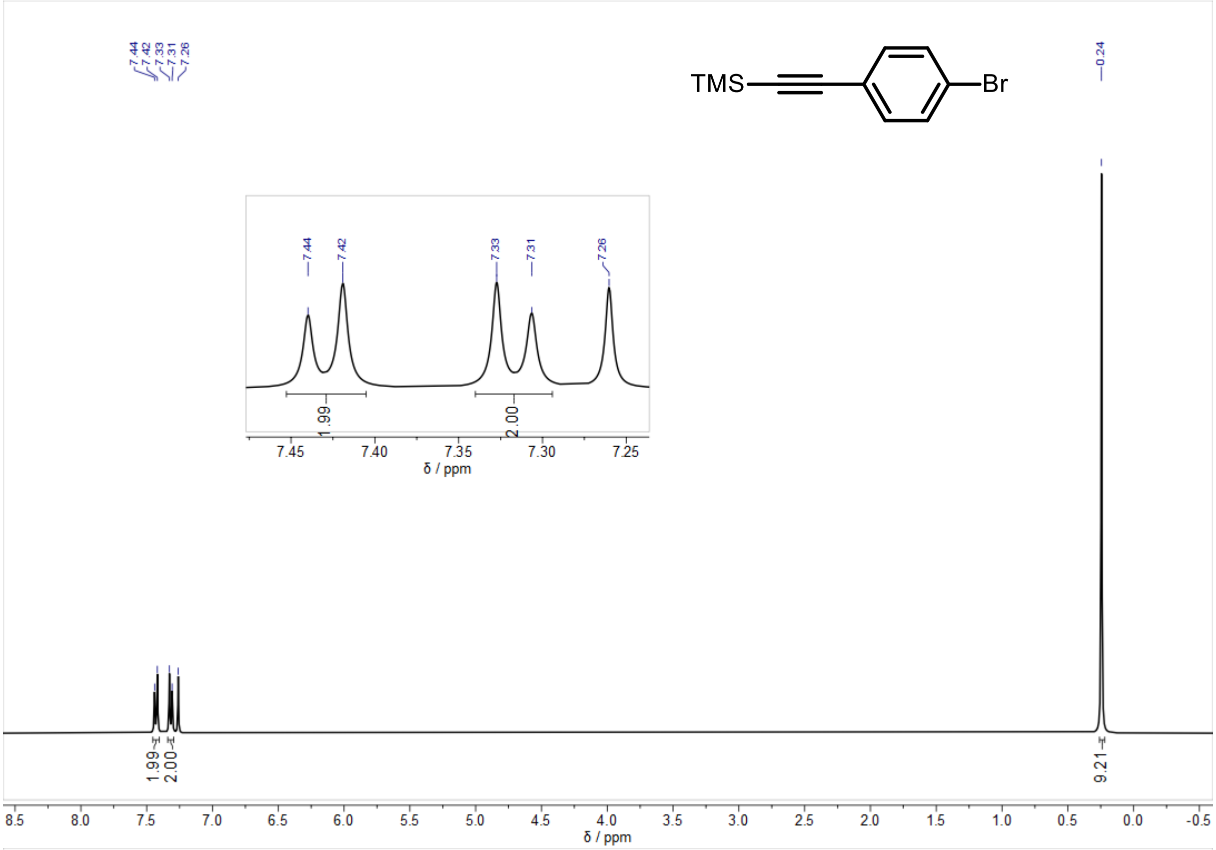
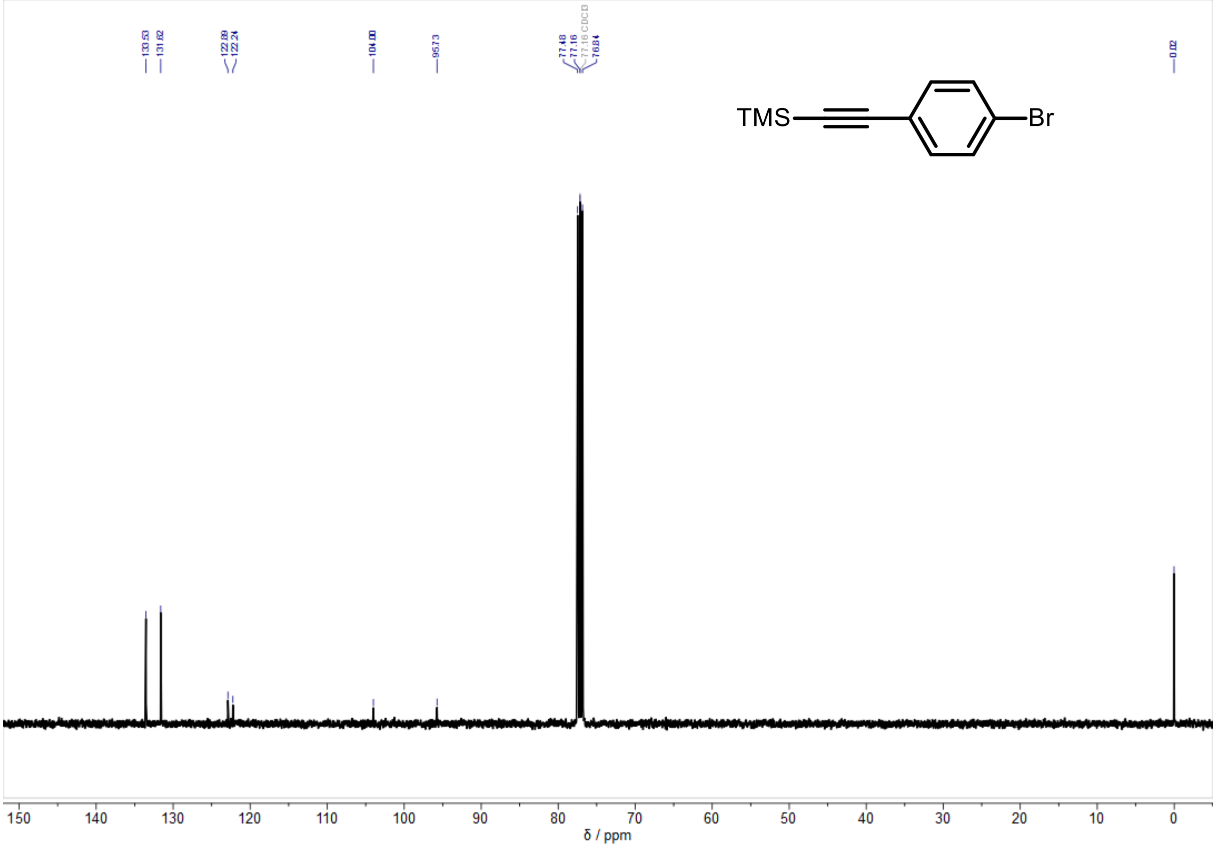
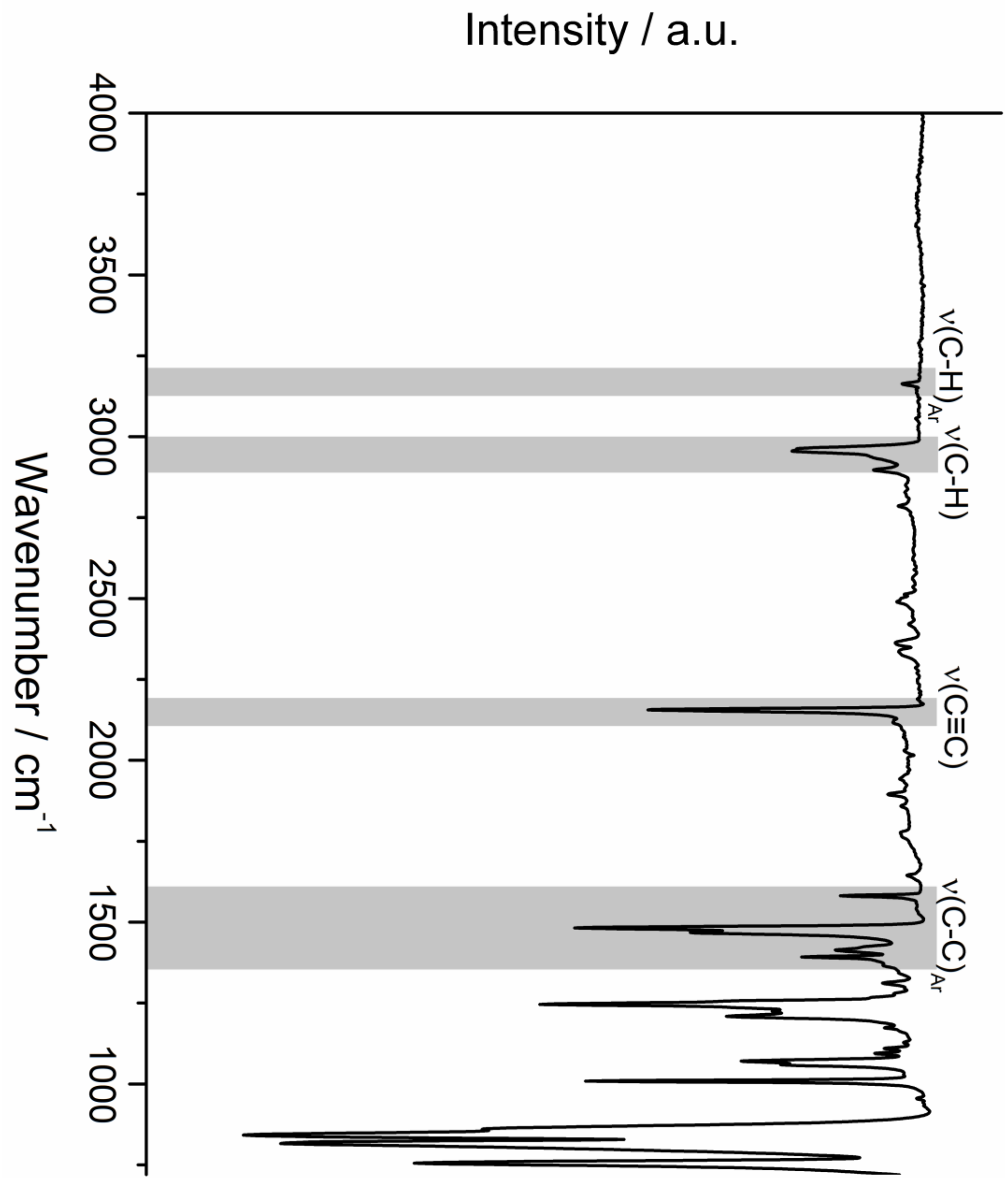
ν(C-H)$_{Ar}$
ν(C≡C)
ν(C-C)$_{Ar}$

((4-bromophenyl)ethynyl)trimethylsilane 2



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Wavenumber / cm^{-1}
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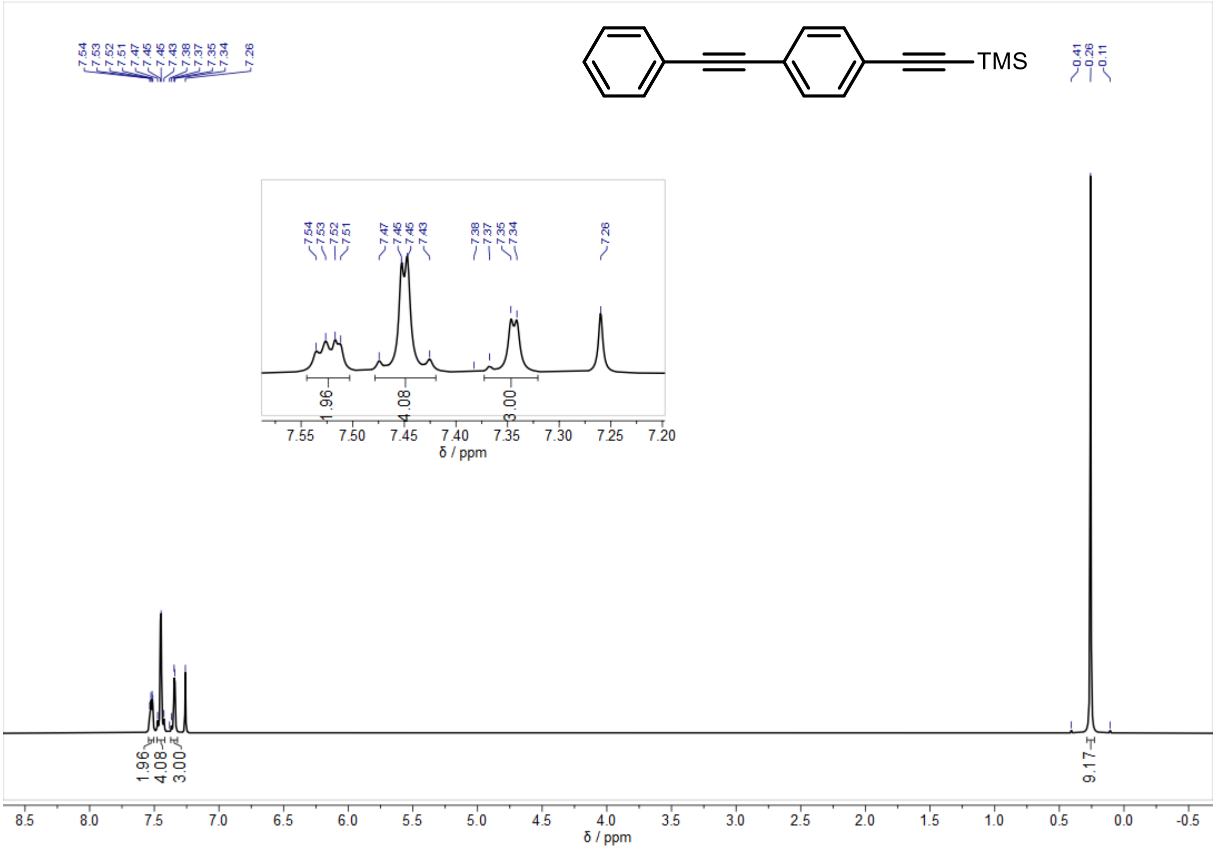
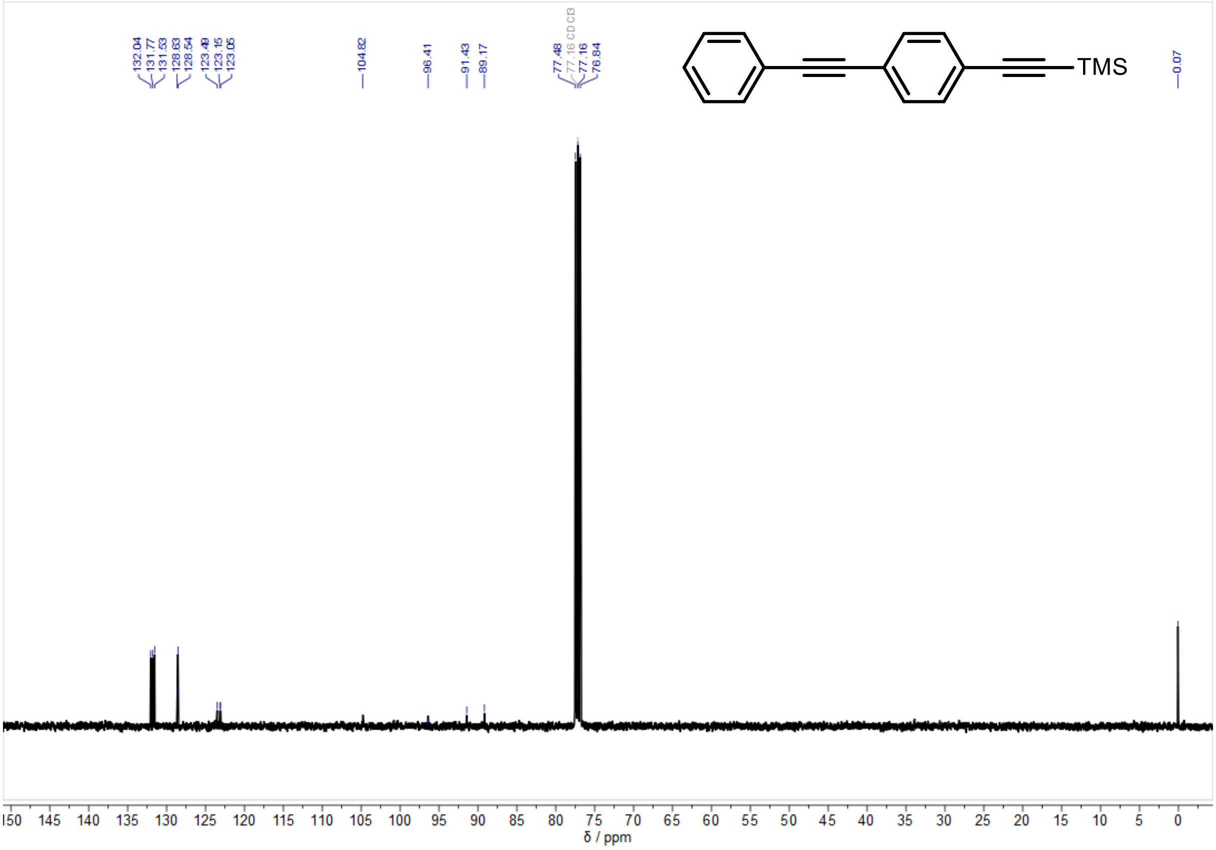
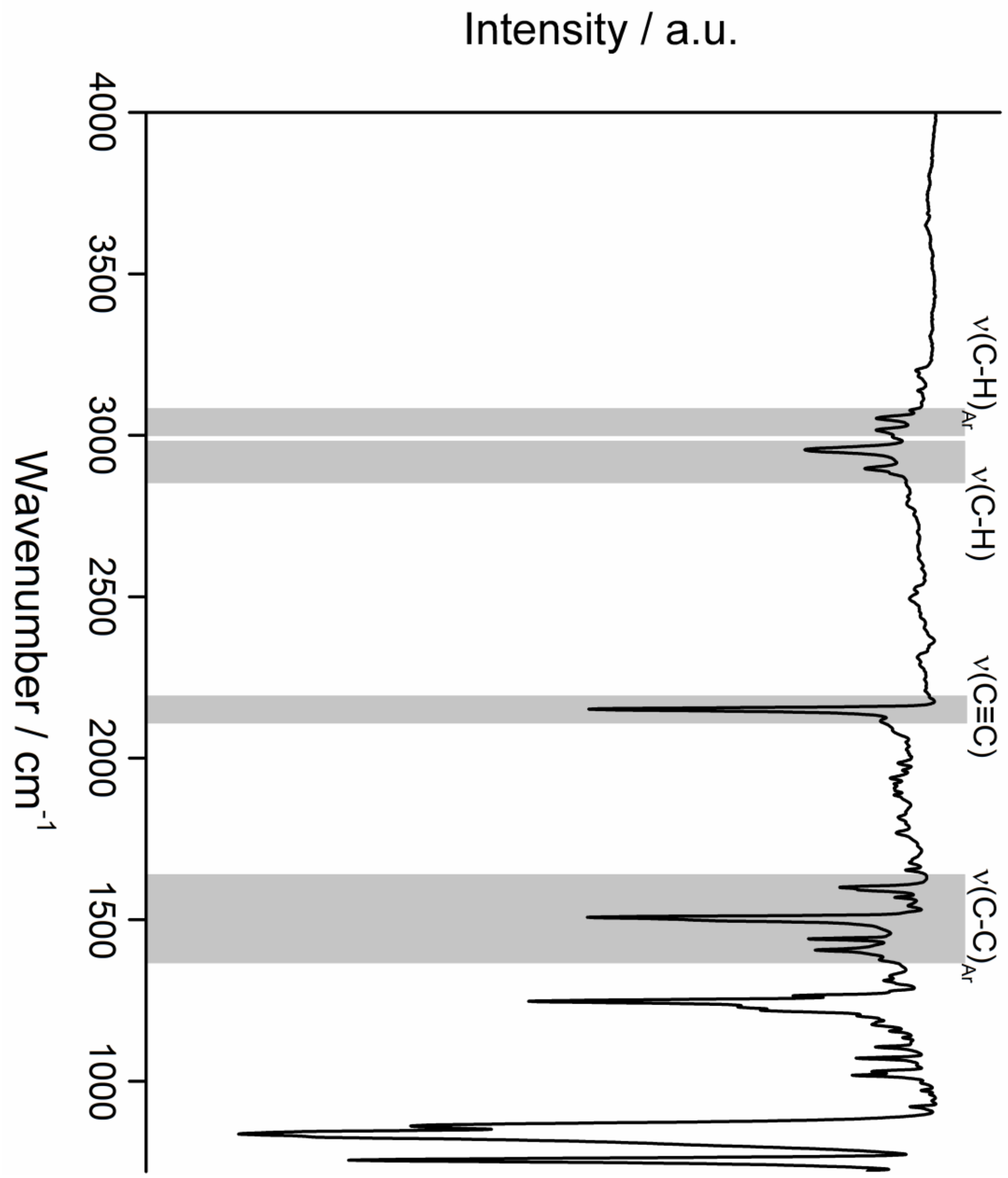
ν(C≡C)
ν(C-C)$_{Ar}$

1-(phenylethynyl)-4-[(trimethylsilyl)ethynyl]benzene 3



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Wavenumber / cm^{-1}
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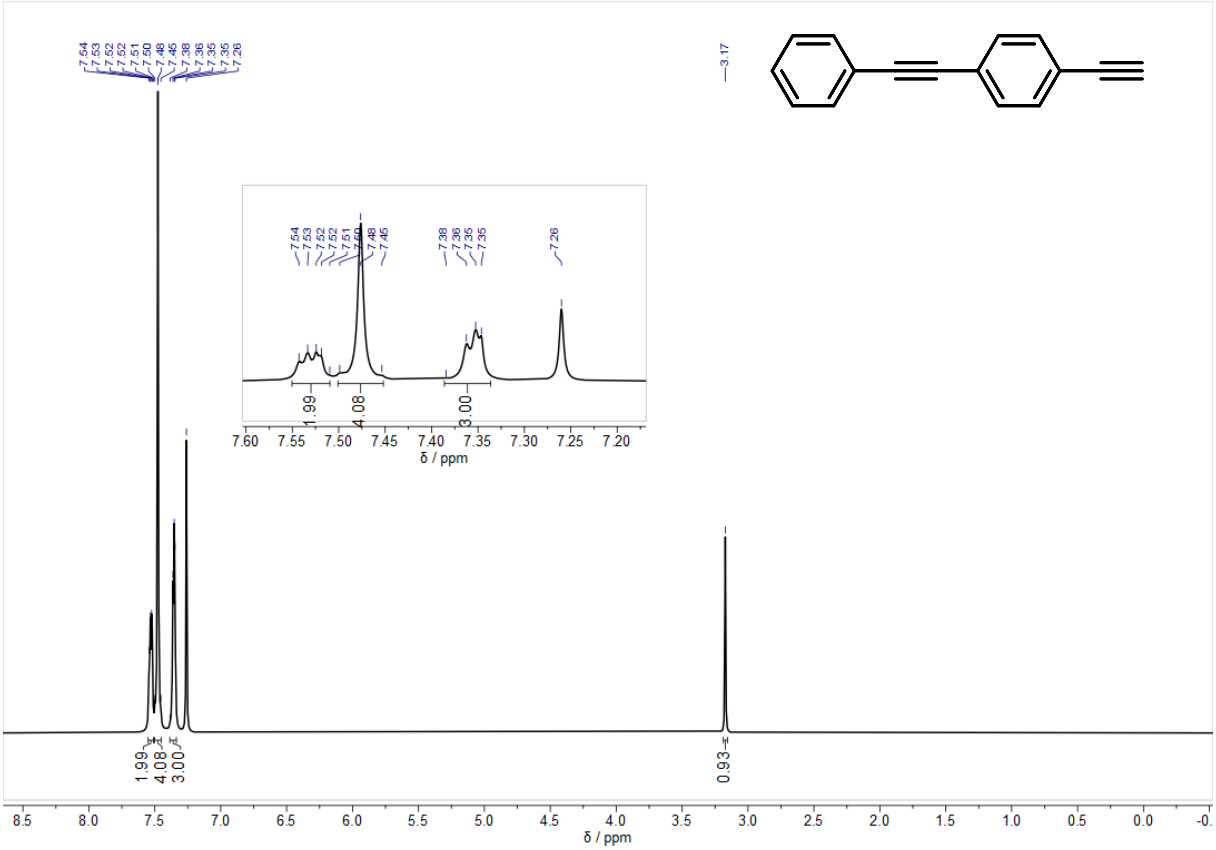
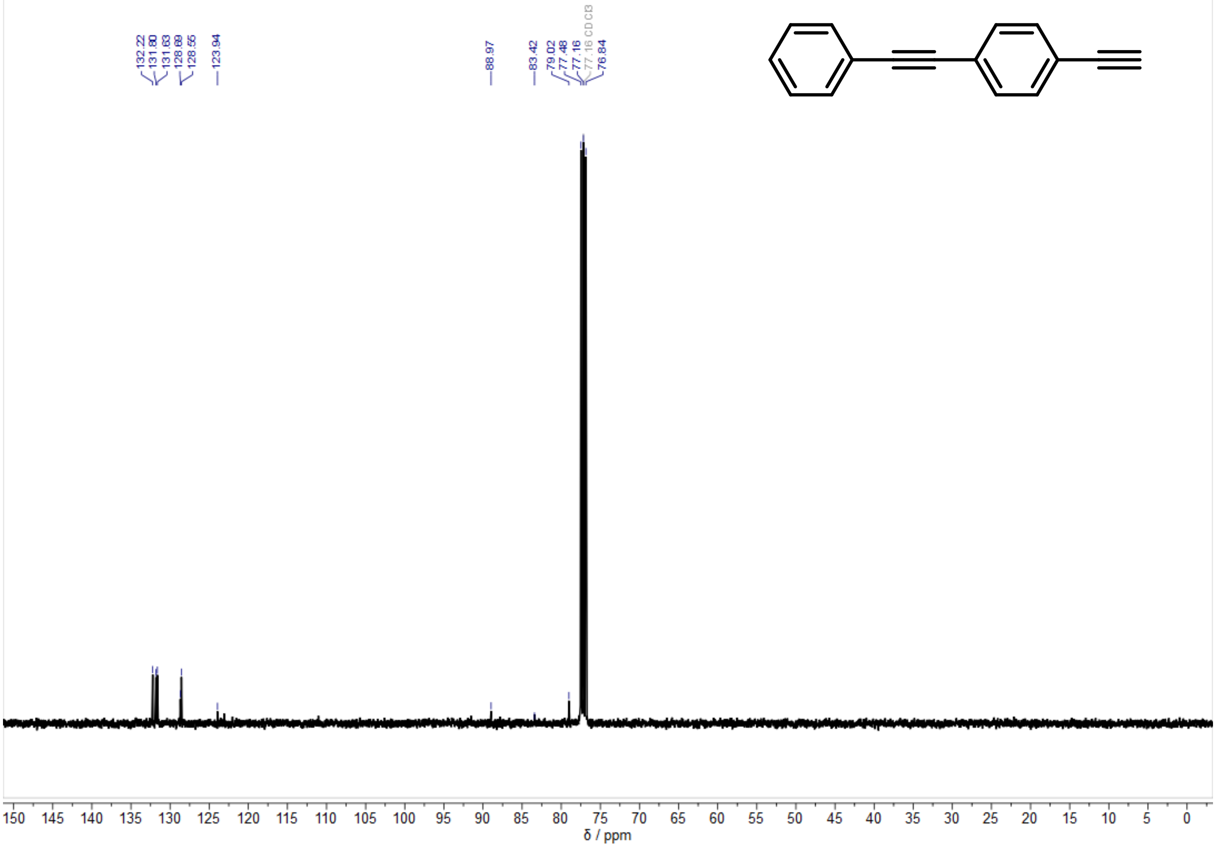
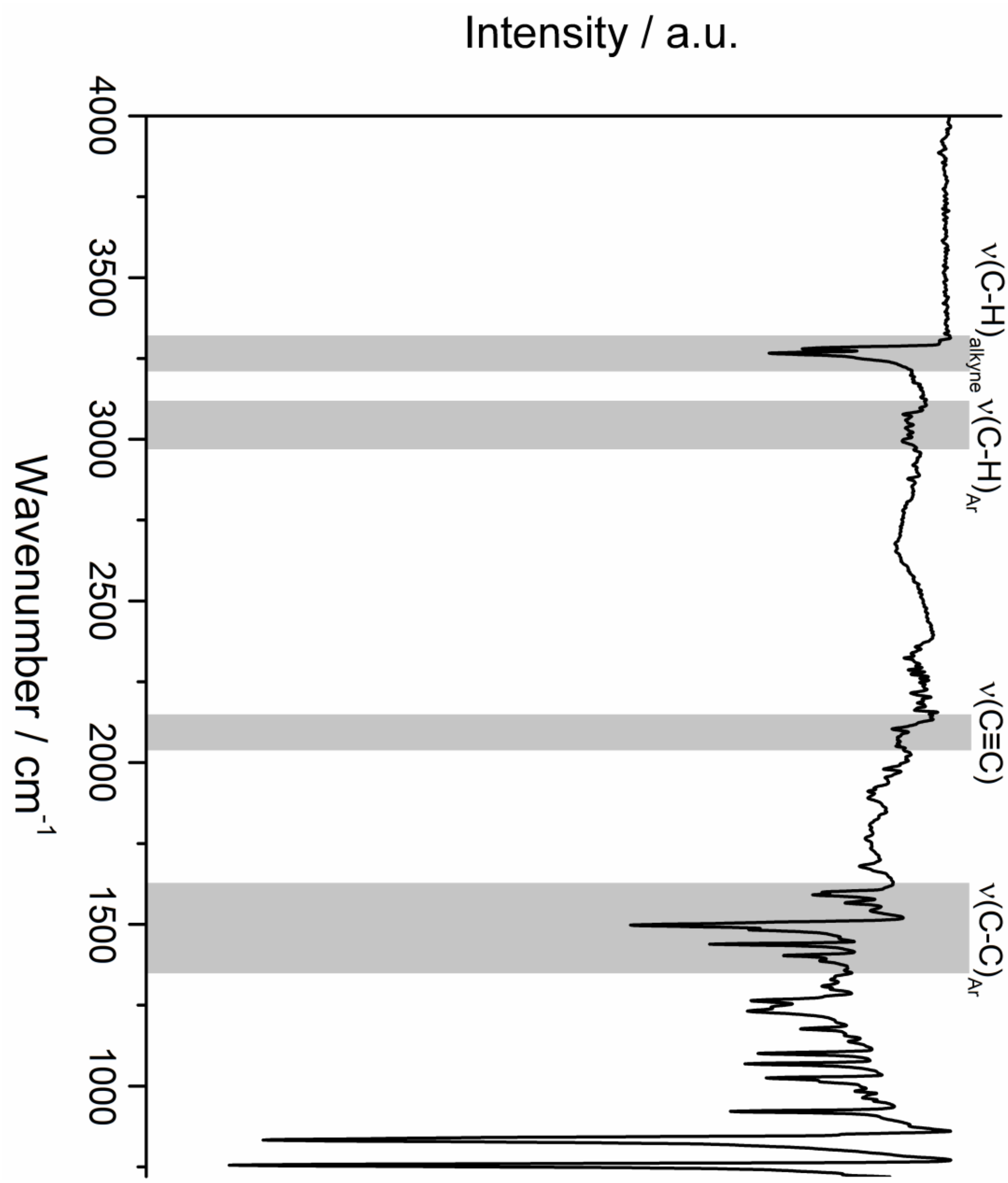
ν(C-H)
ν(C≡C)
ν(C-C)$_{Ar}$

1-ethynyl-4-(phenylethynyl)benzene 4



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Wavenumber / cm^{-1}
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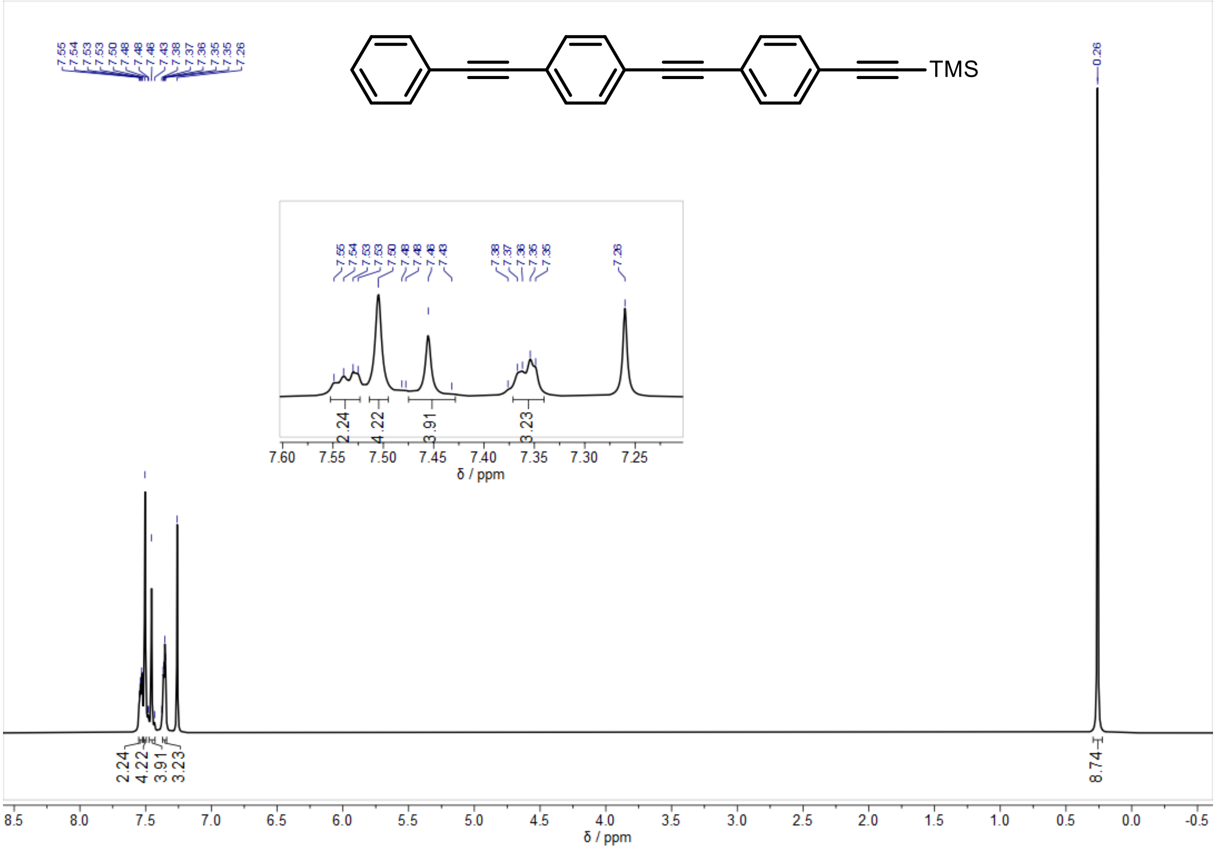
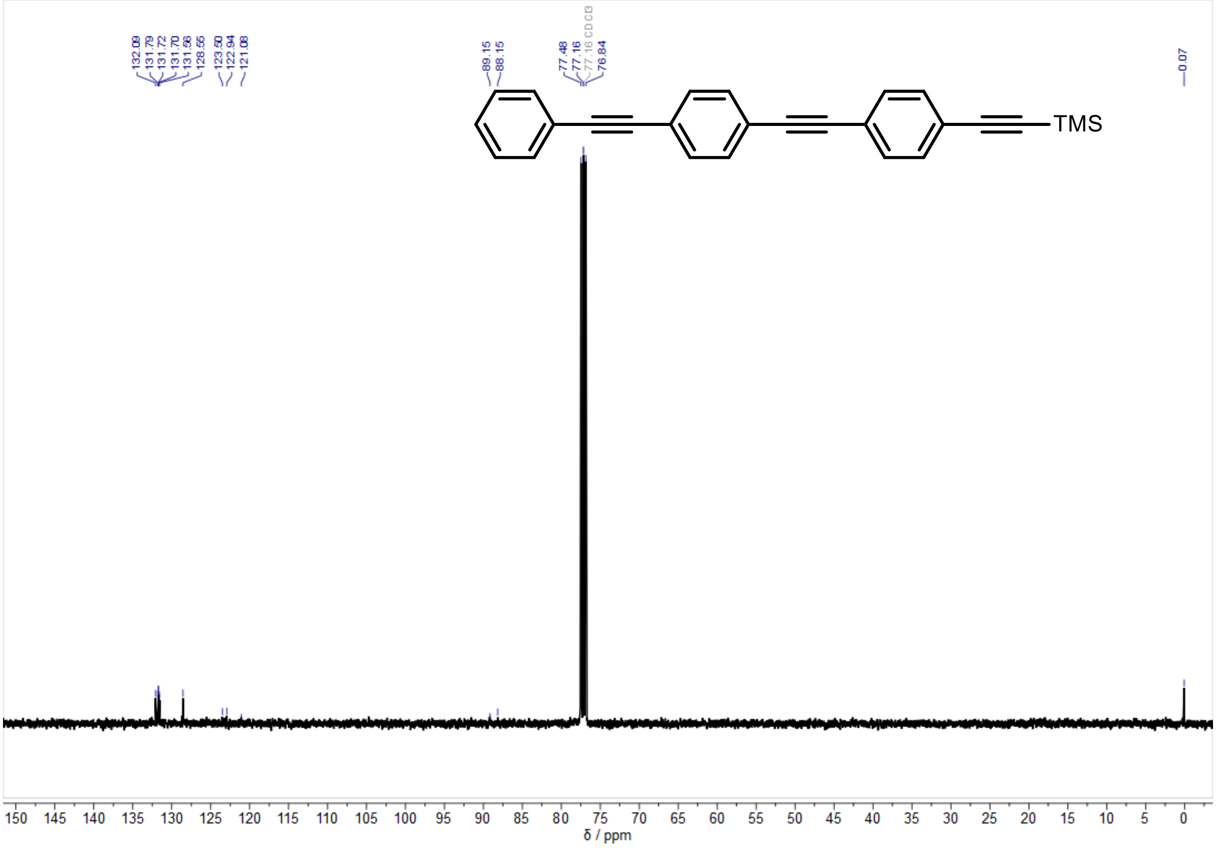
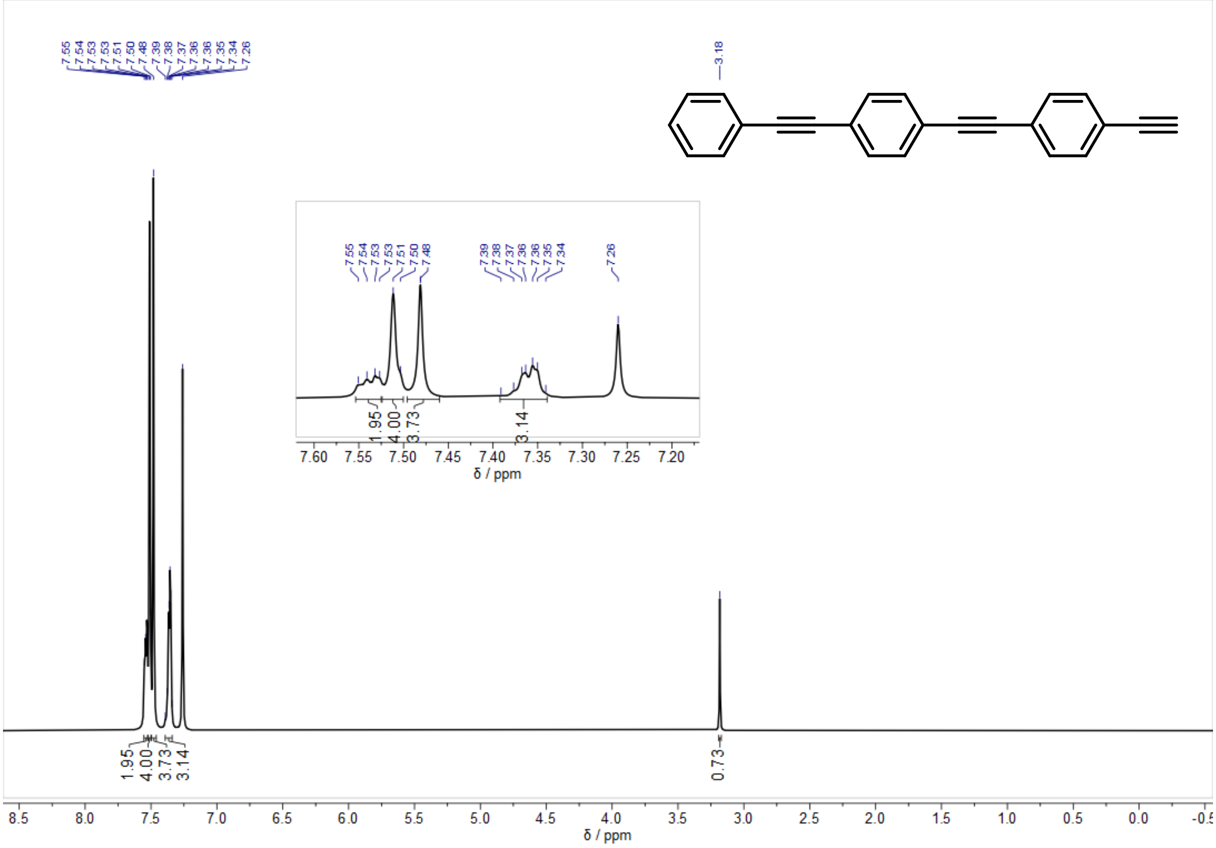
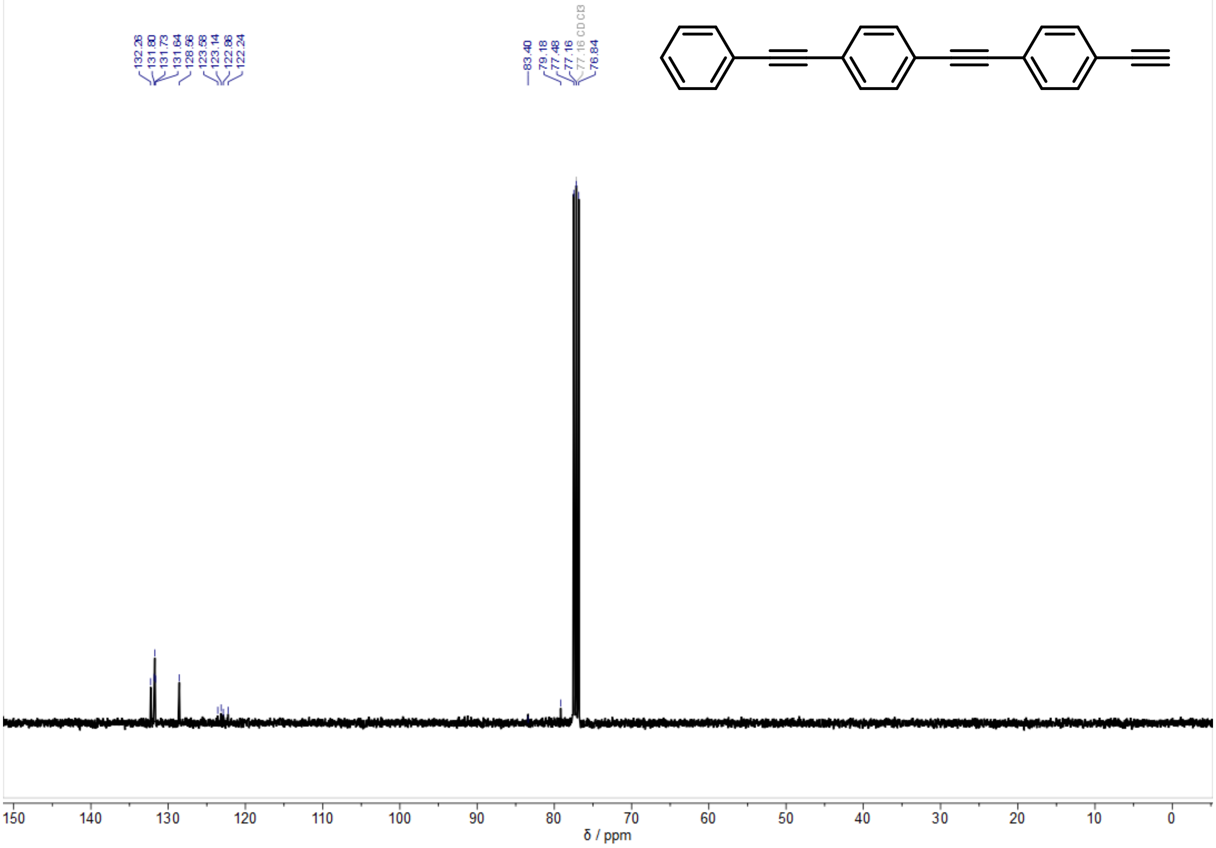
trimethyl[4-(4-(phenylethynyl)phenylethynyl)phenylethynyl]silane 5

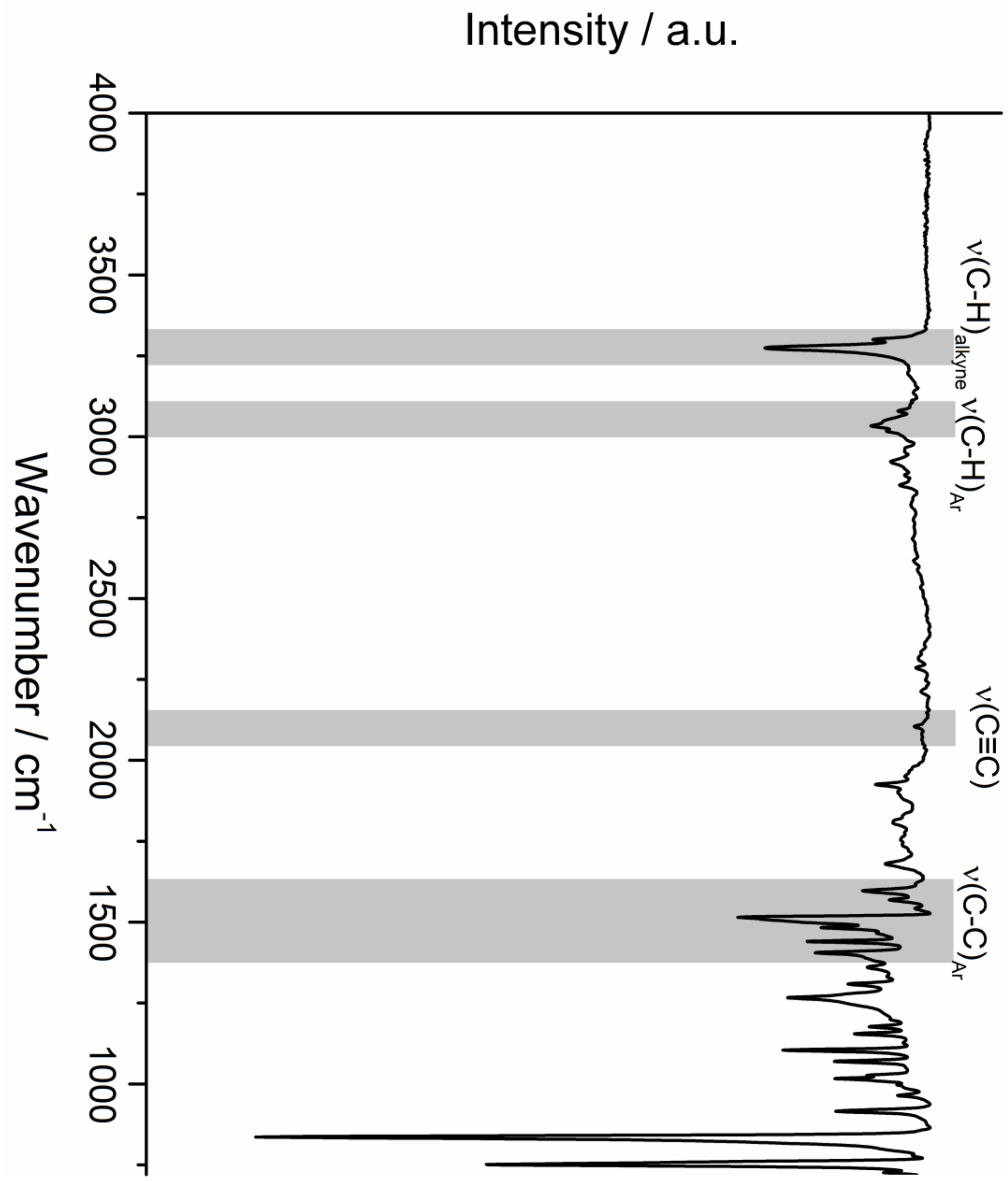




4-(2-(4-ethynylphenyl)-ethynyl)-1-(2-phenylethynyl)benzene 6



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Wavenumber / cm^{-1}
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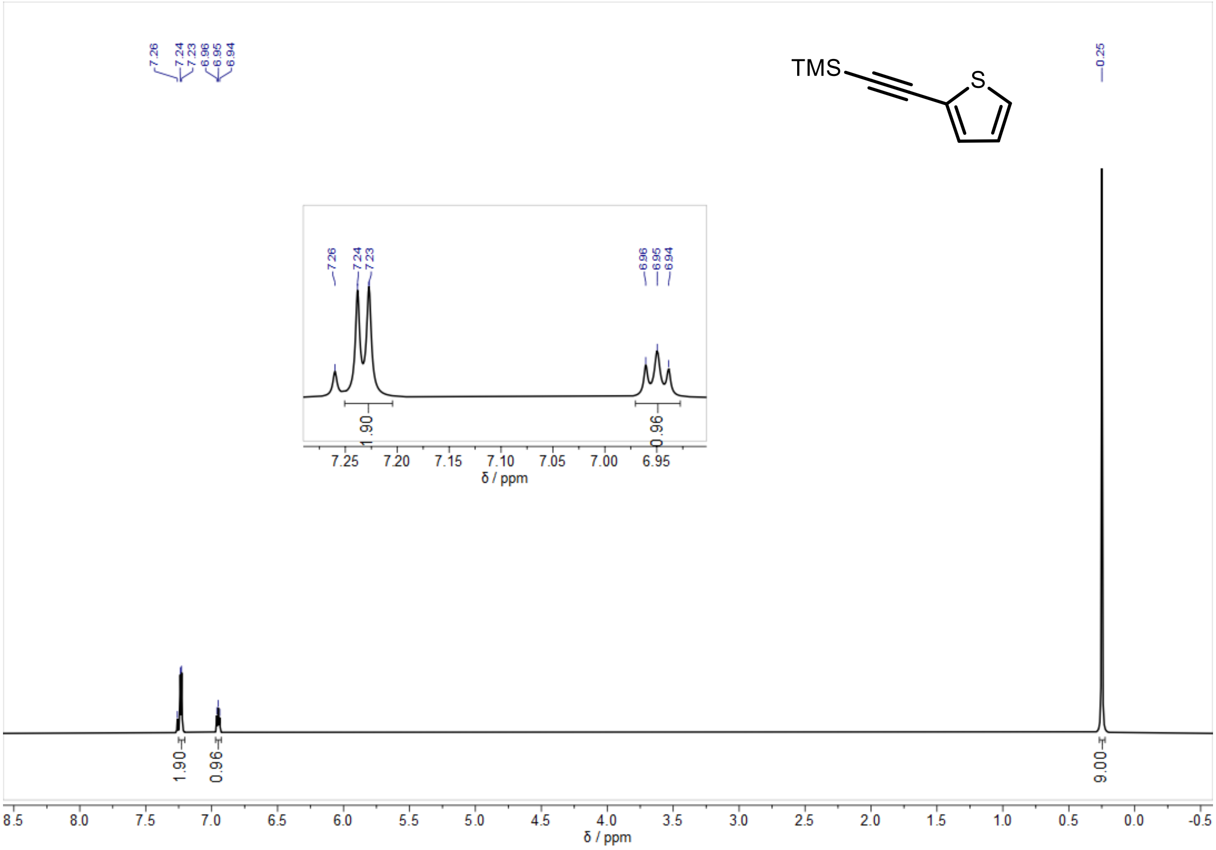
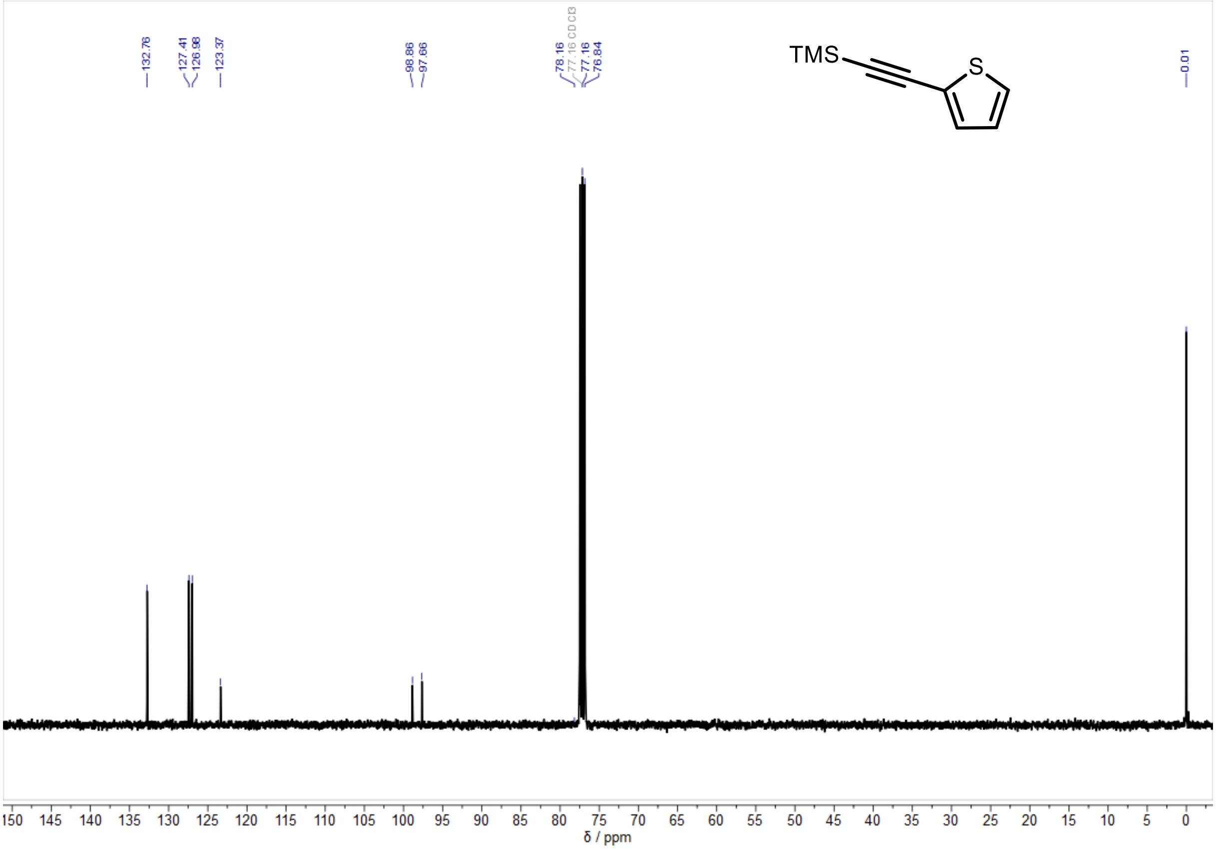
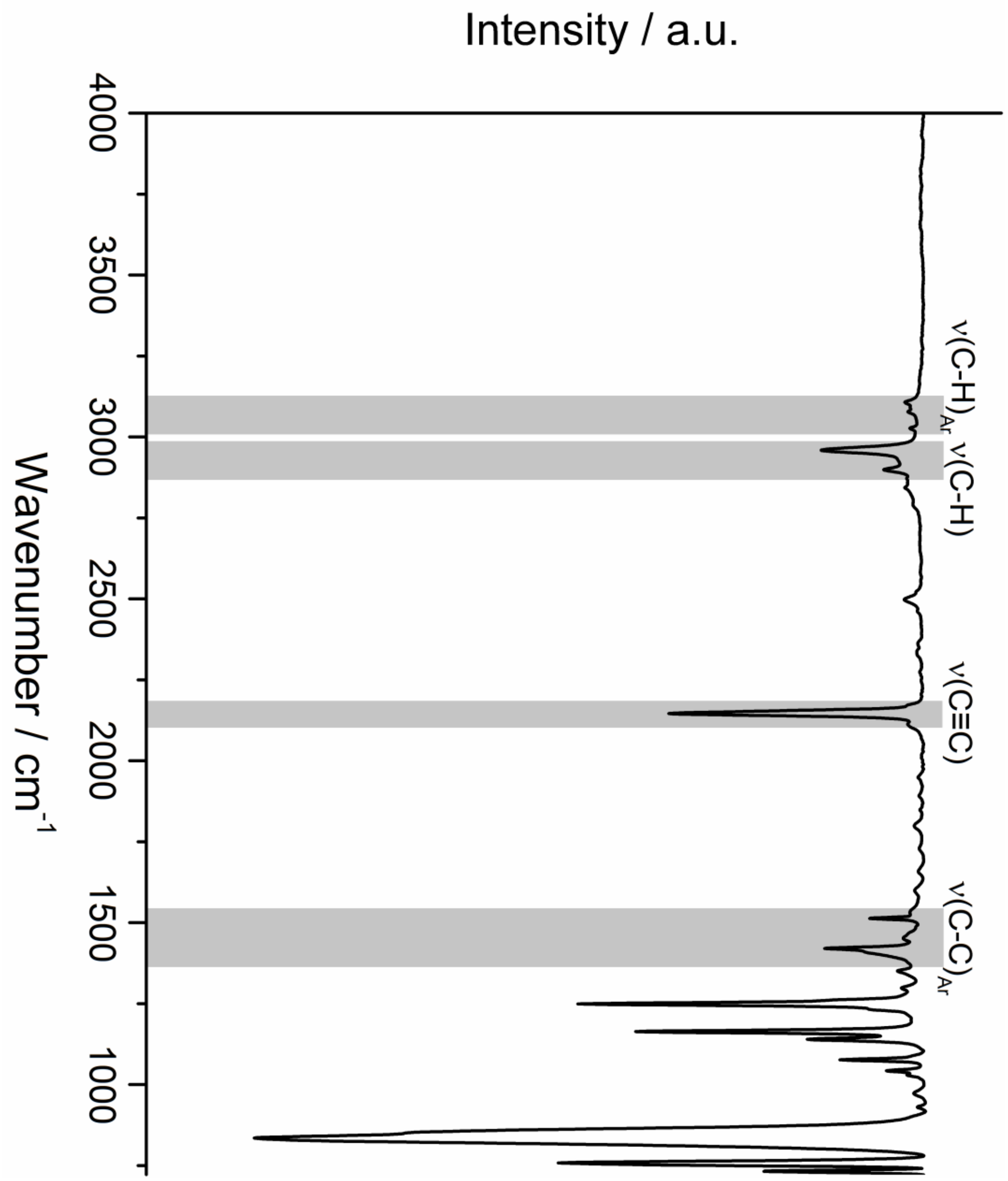
2-[(Trimethylsilyl)ethynyl]thiophene 7



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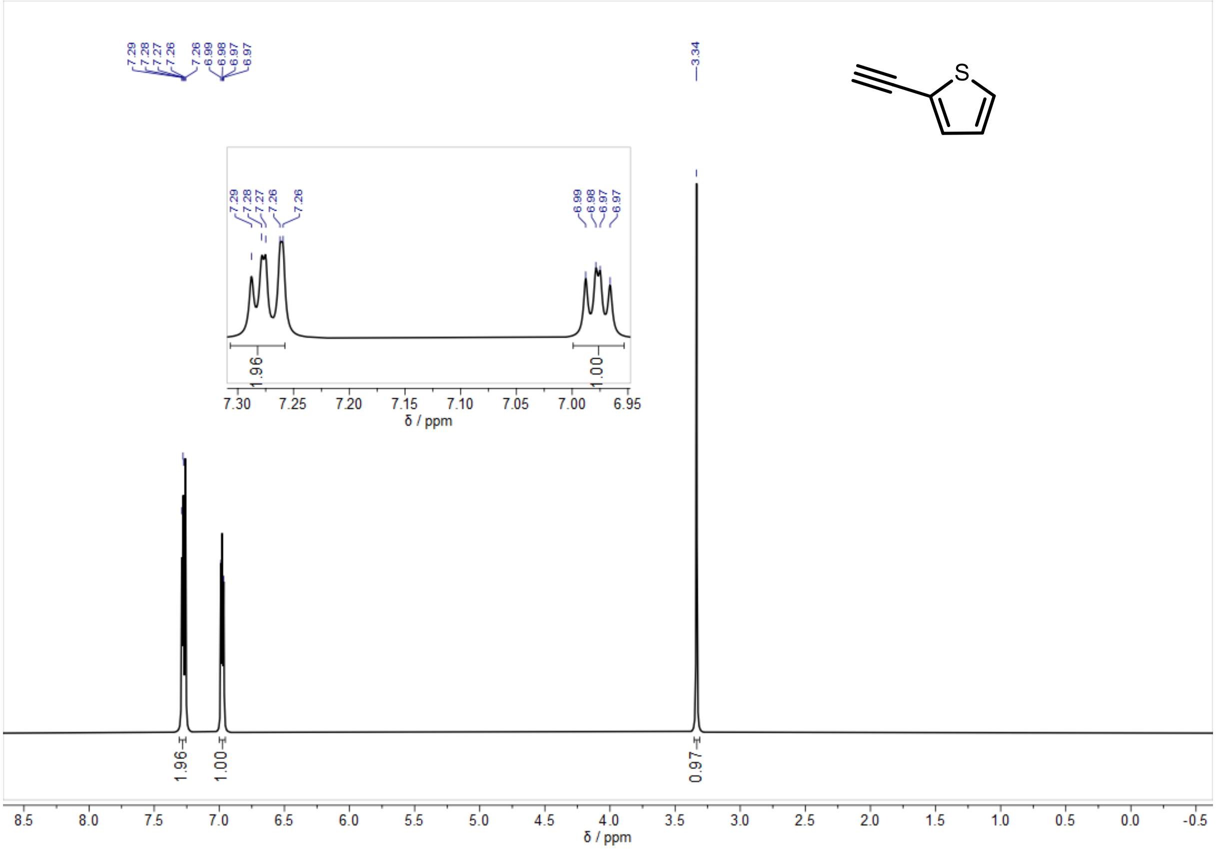
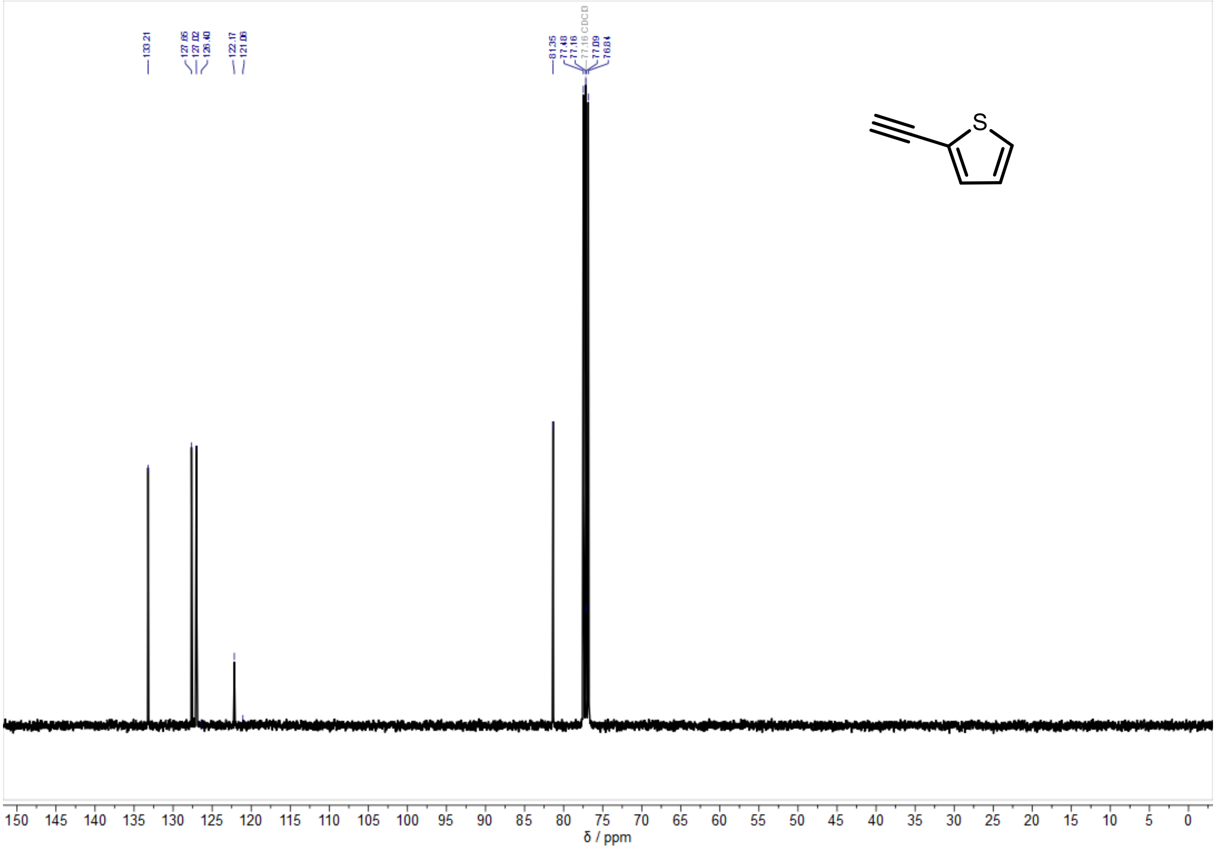
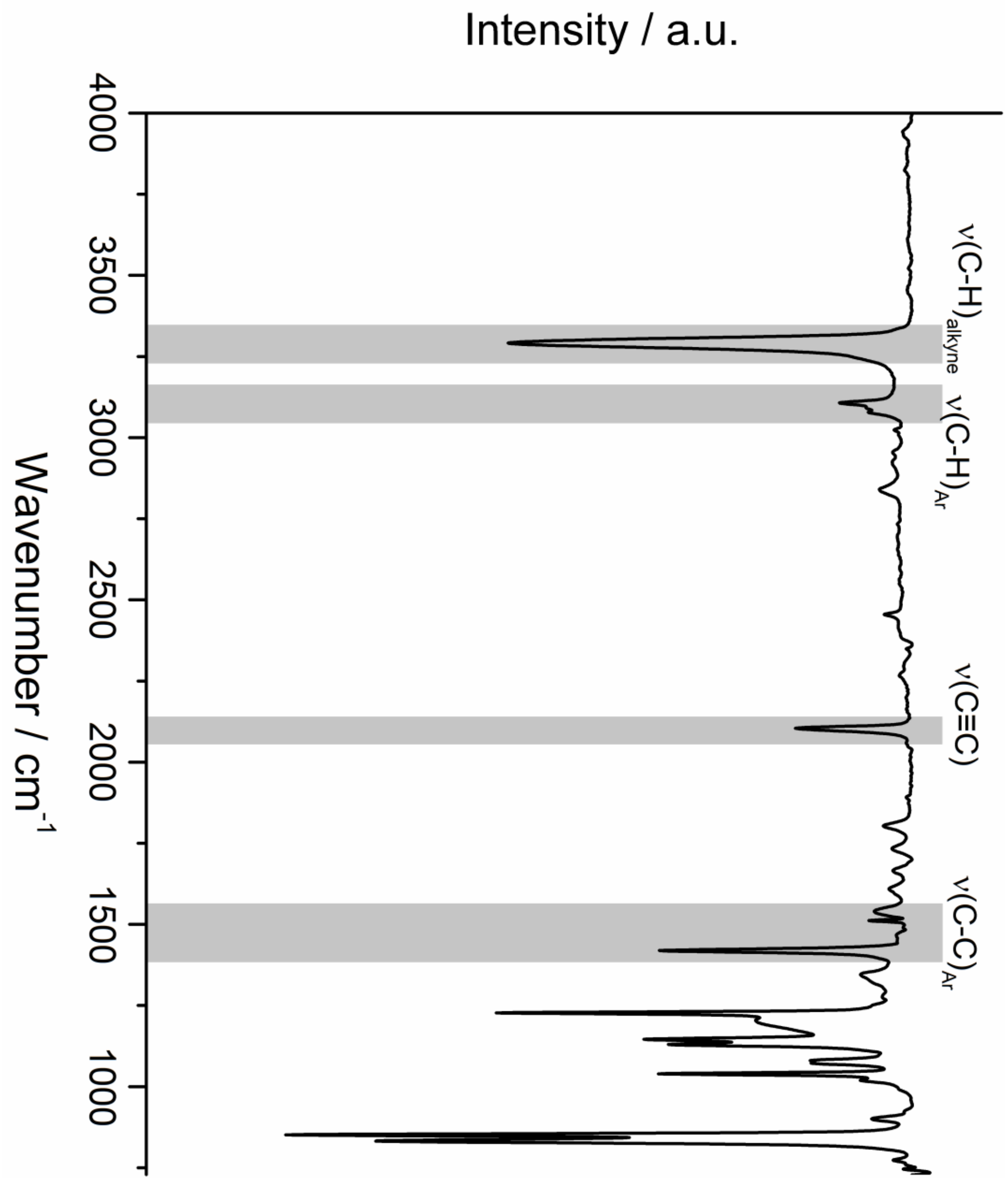
2-ethynylthiophene 8



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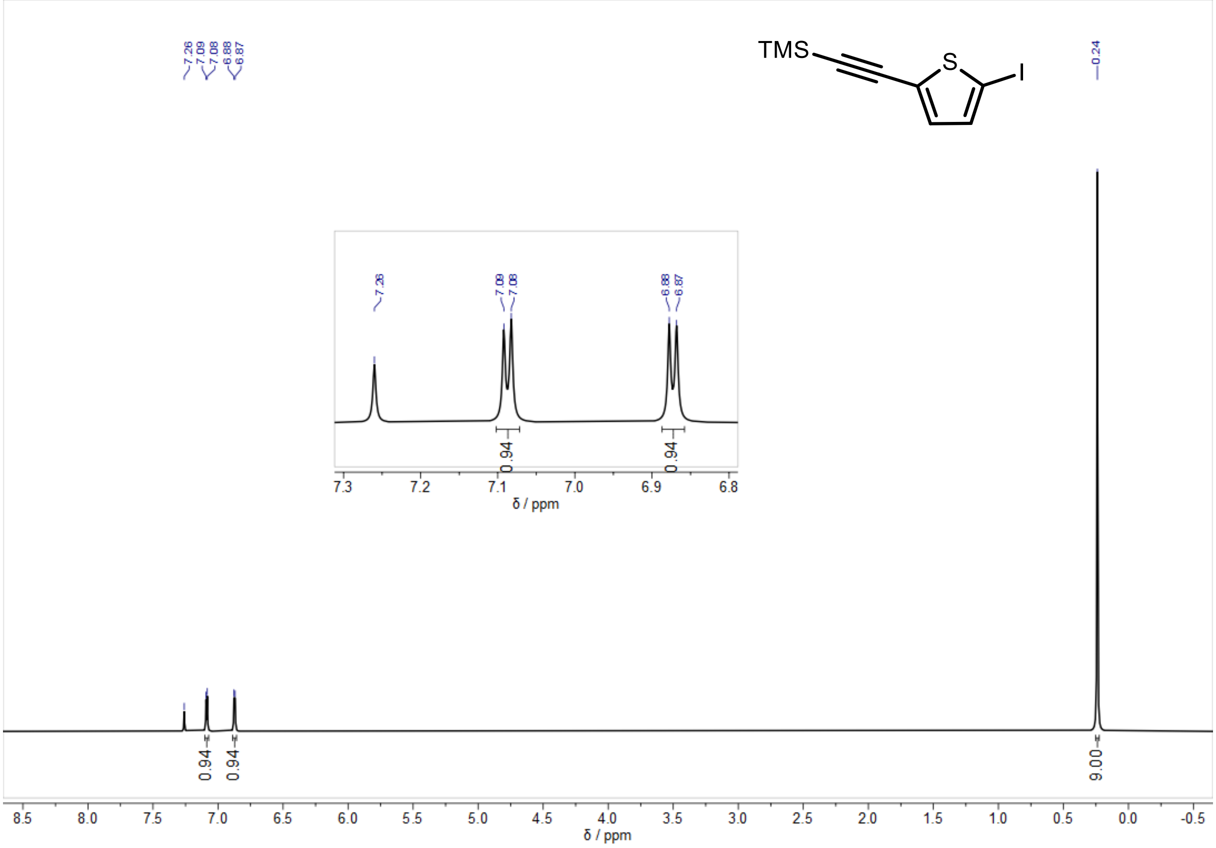
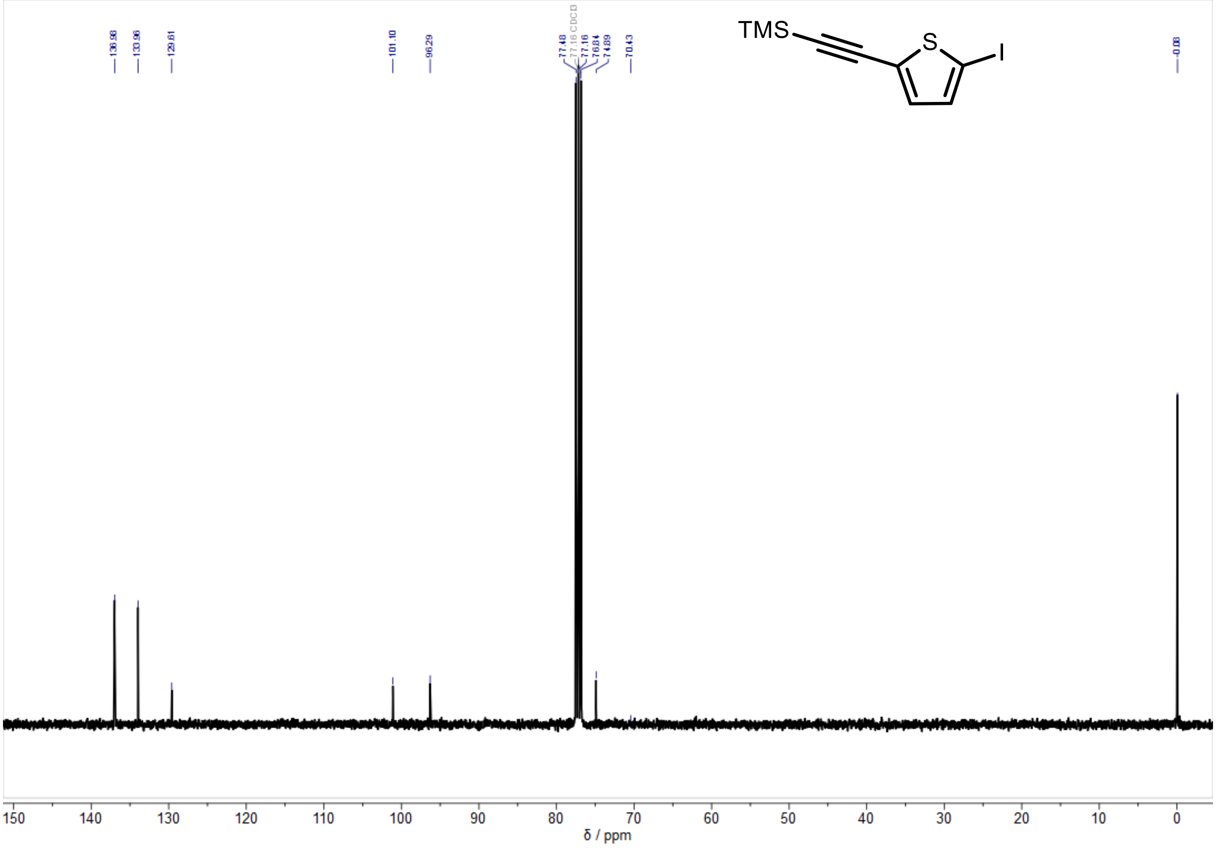
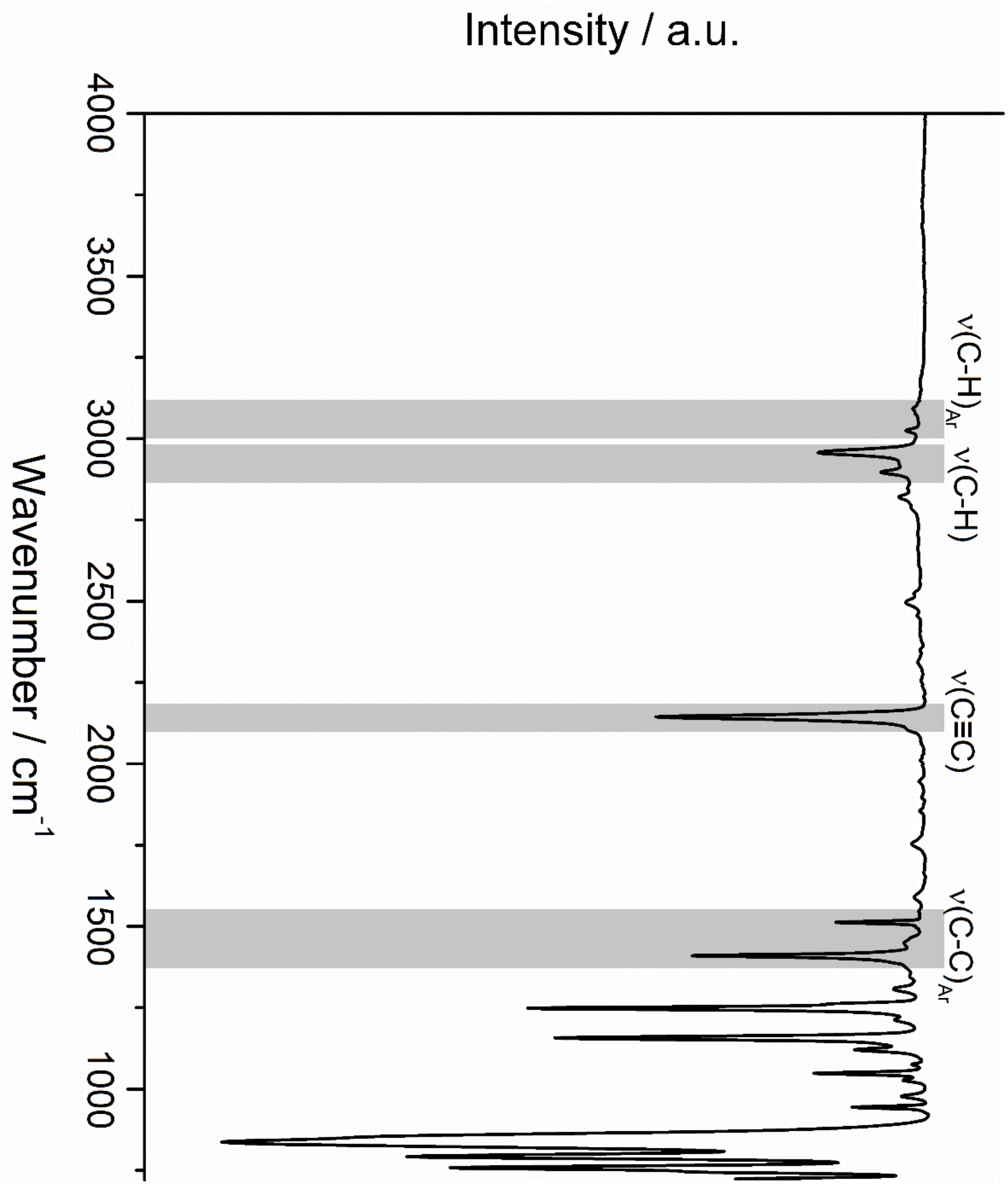
((5-iodothiophen-2-yl)ethynyl)trimethylsilane 9



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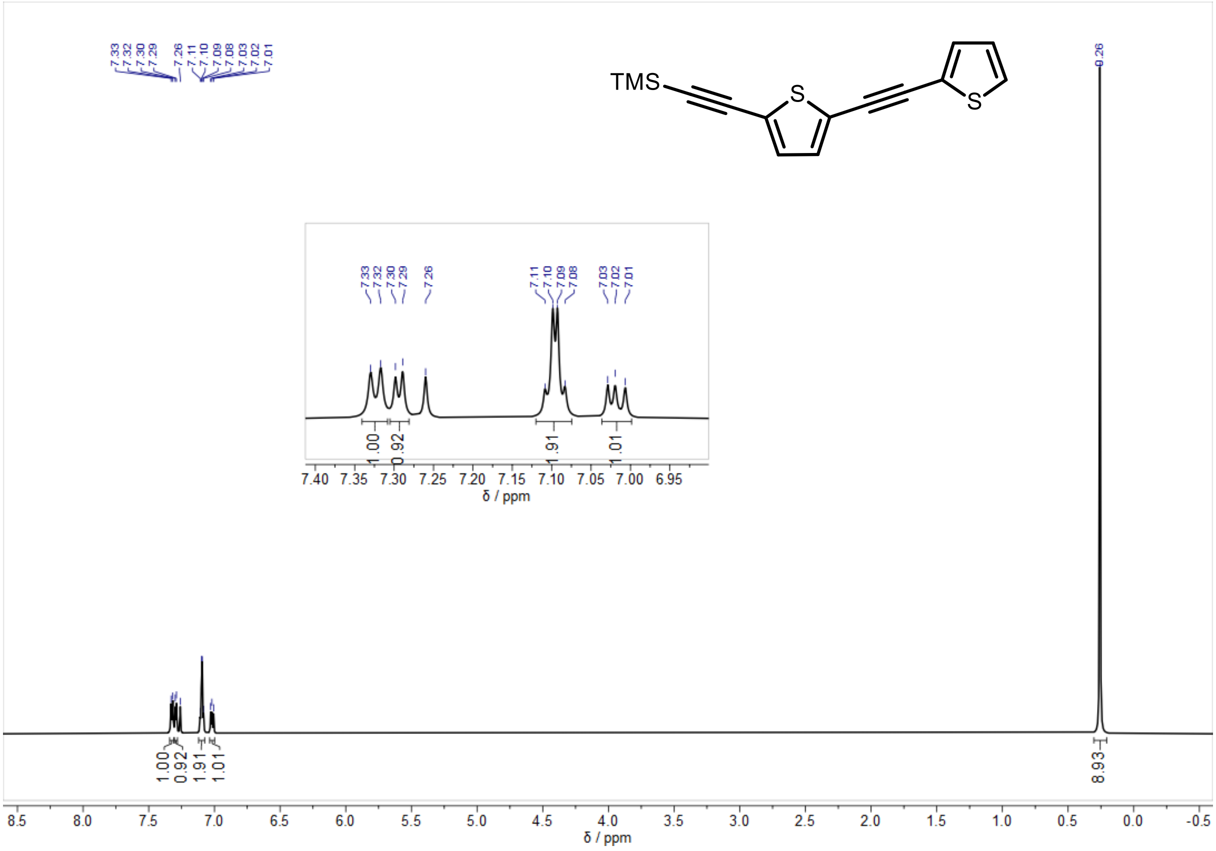
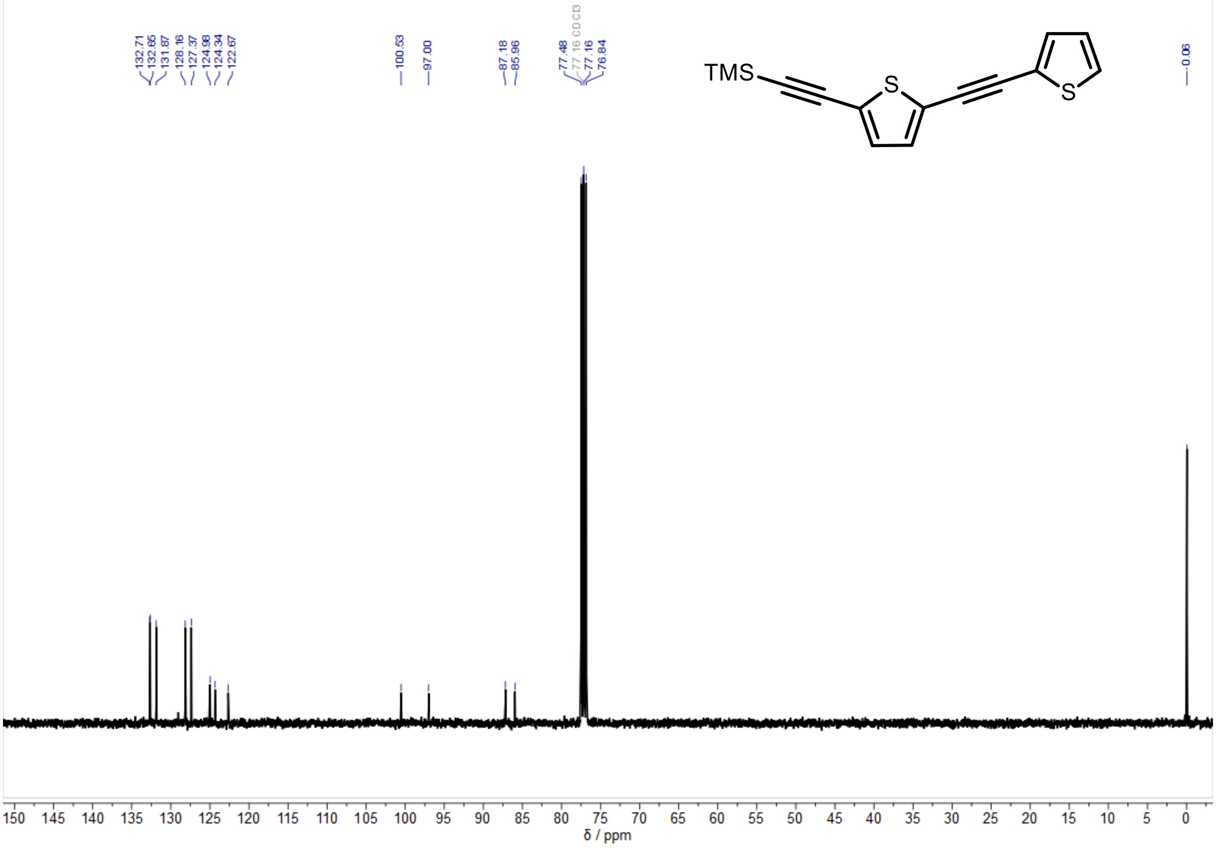
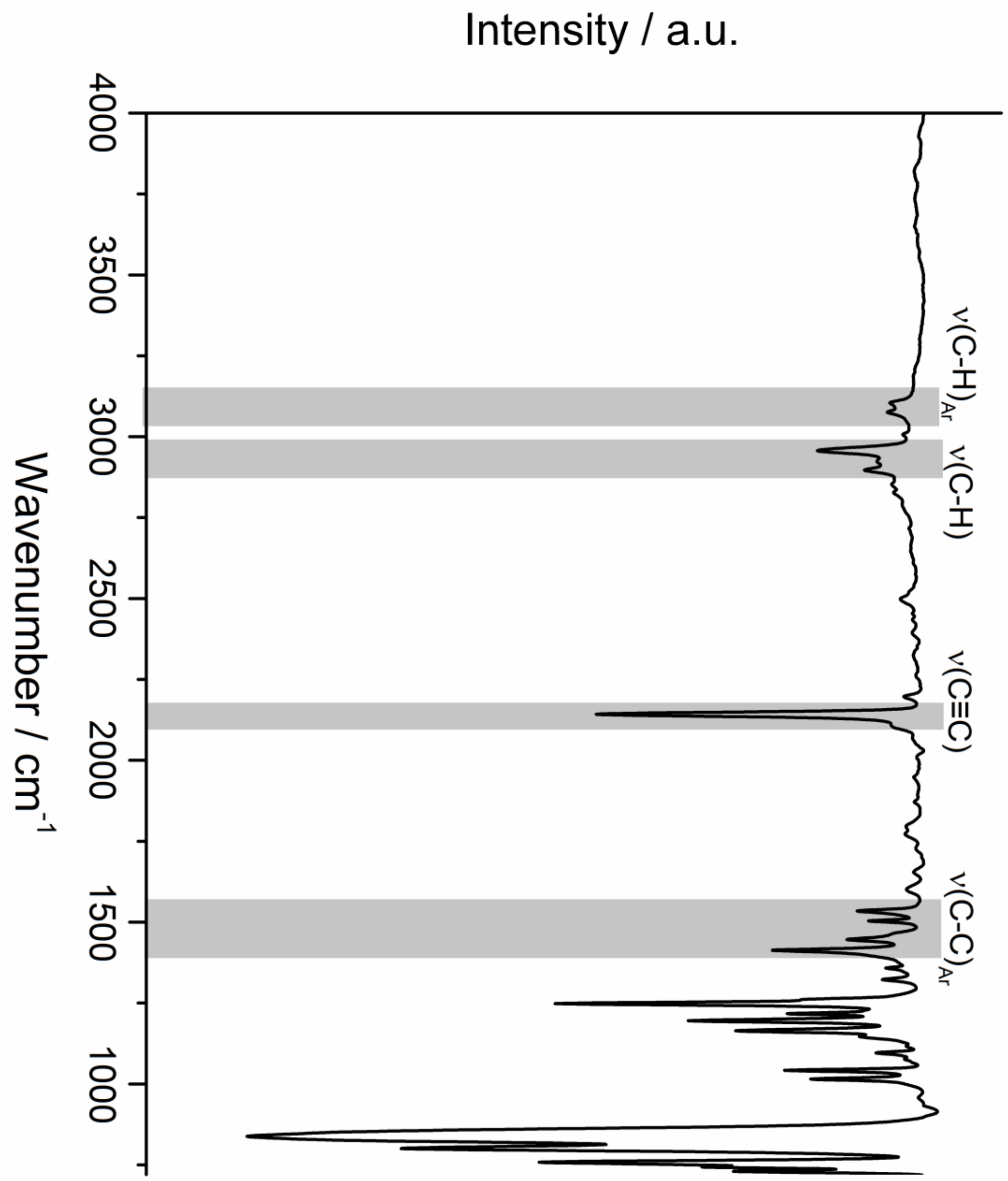
ν(C≡C)
ν(C-C)$_{Ar}$

1-(thiophenethynyl)-4-((trimethylsilyl)ethynyl)thiophene 10



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ν(C≡C)
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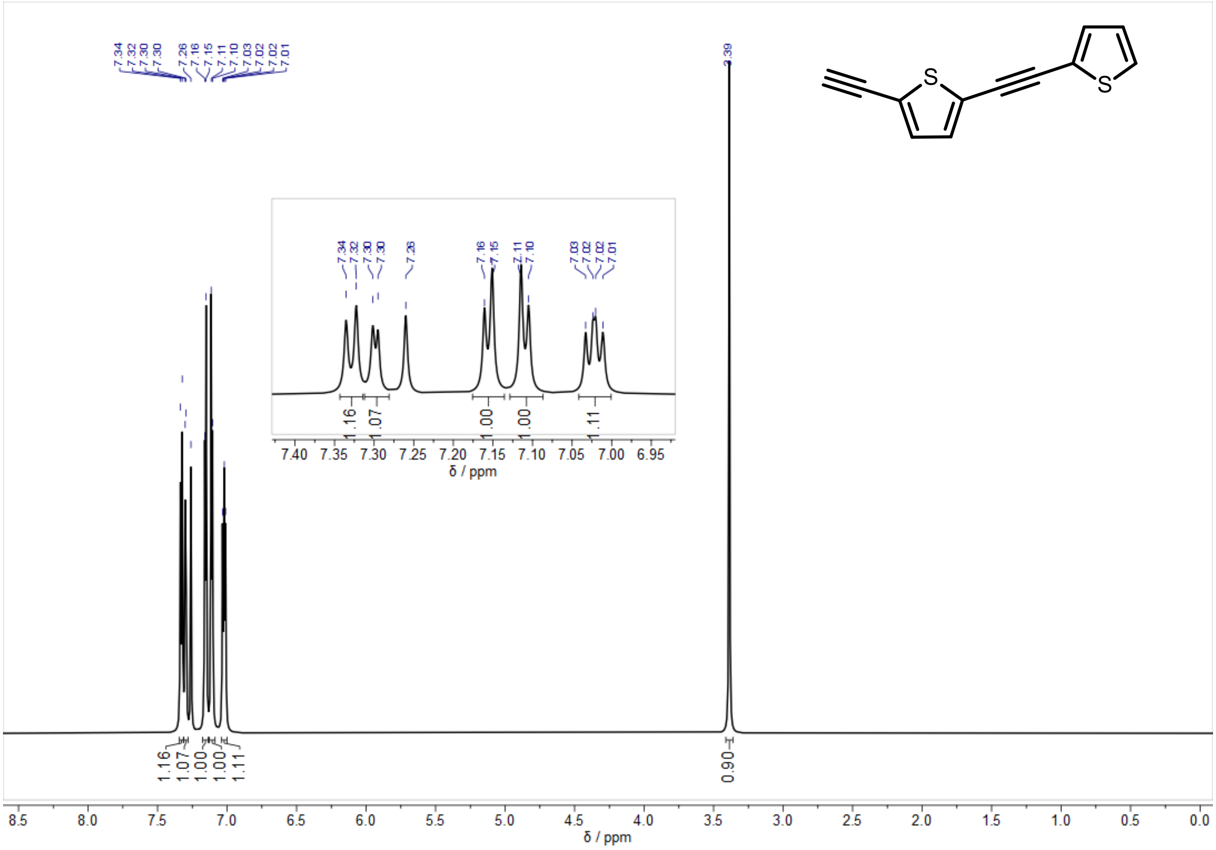
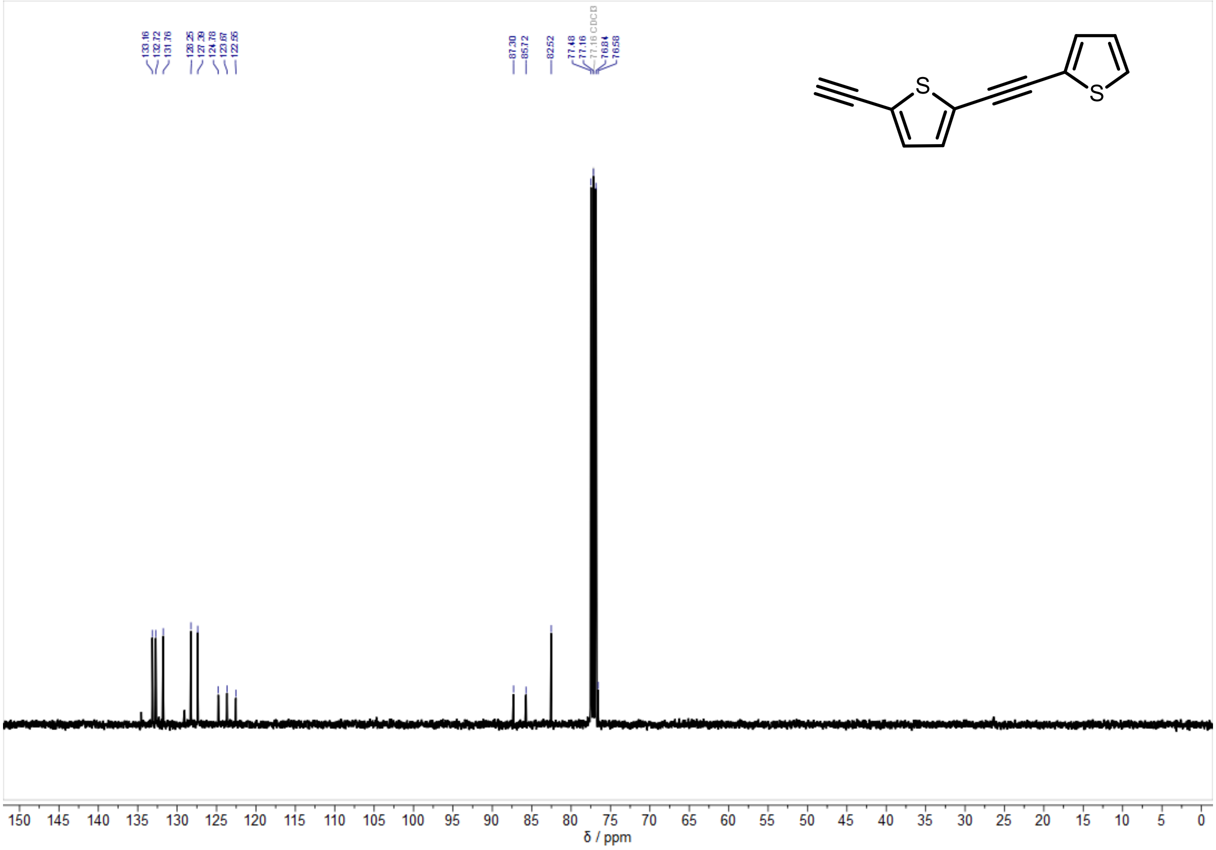
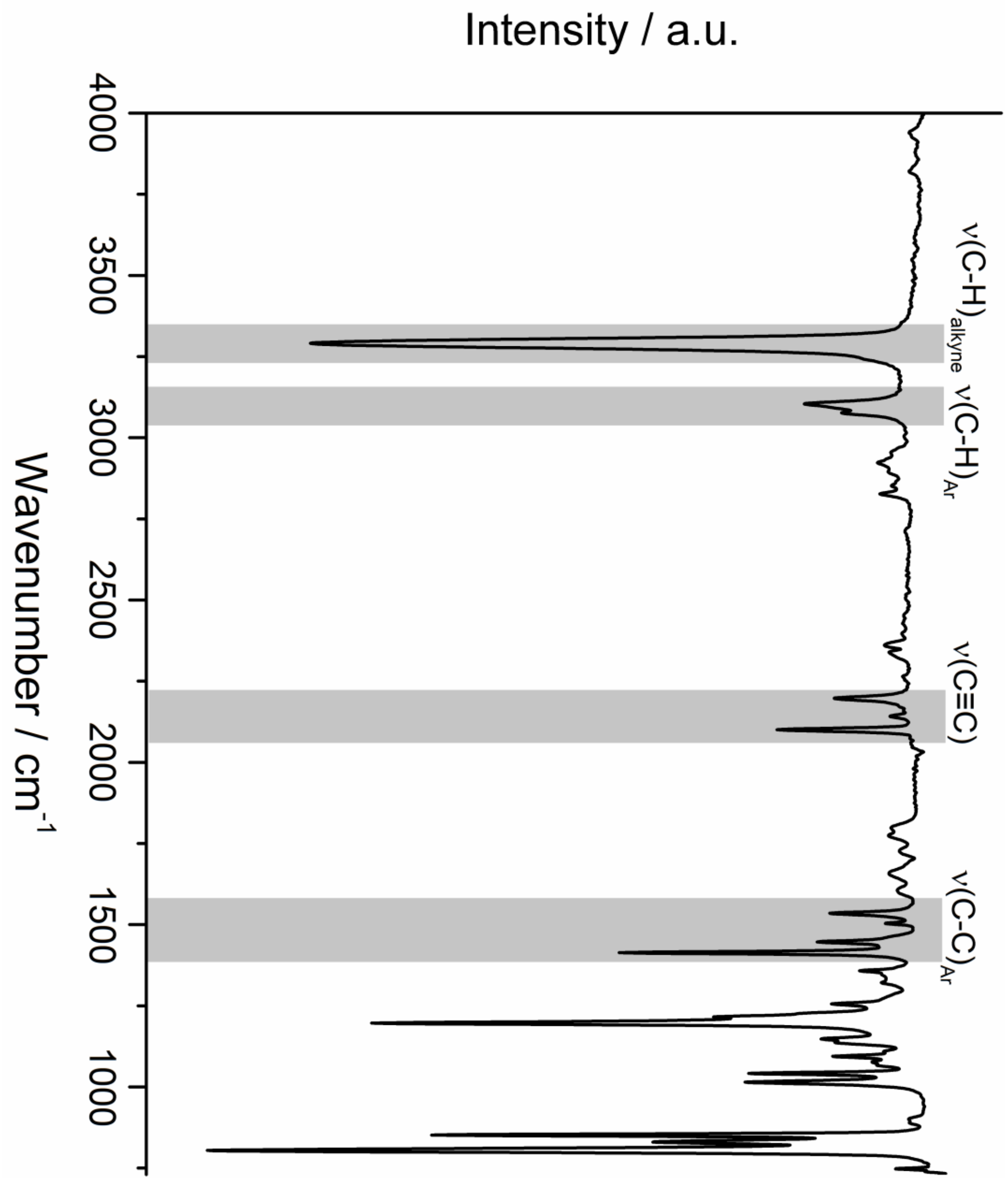
1-(thiophenethynyl)-4-ethynylthiophene 11



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Wavenumber / cm^{-1}
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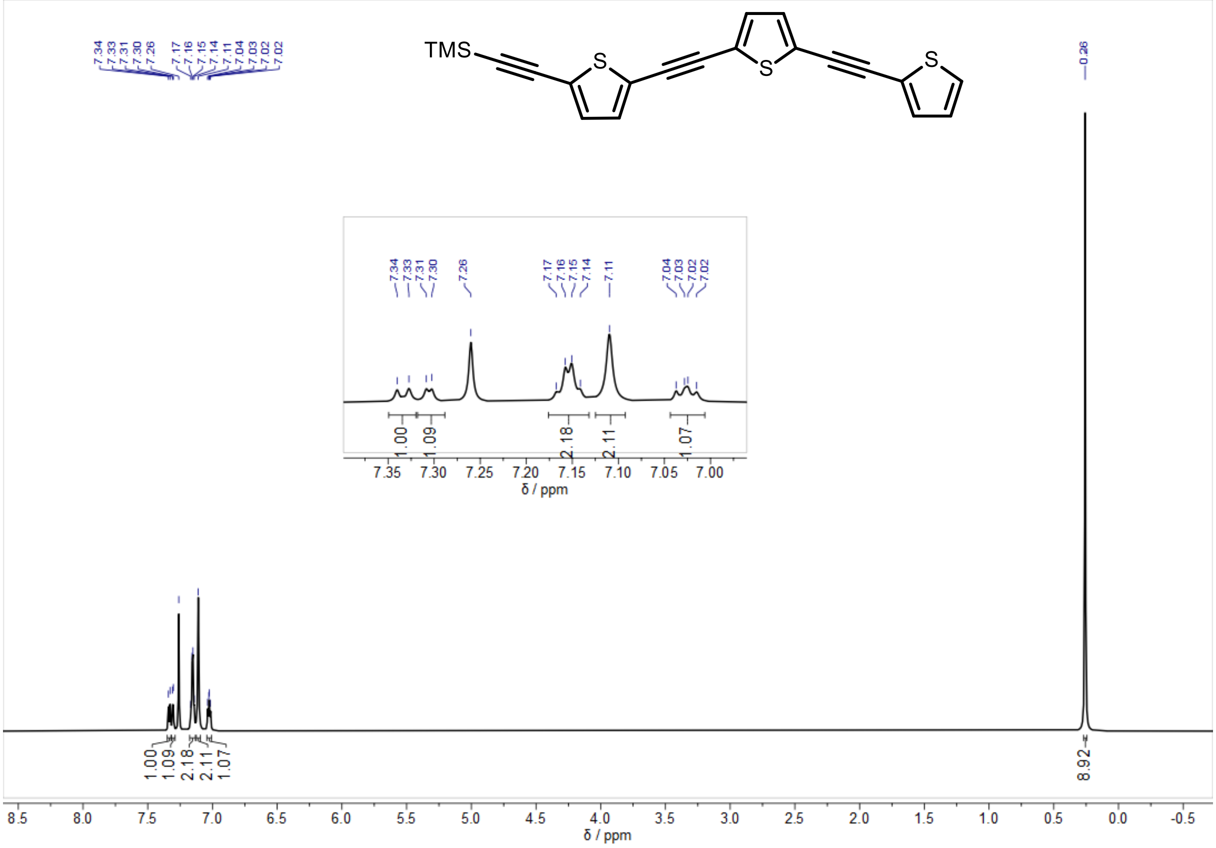
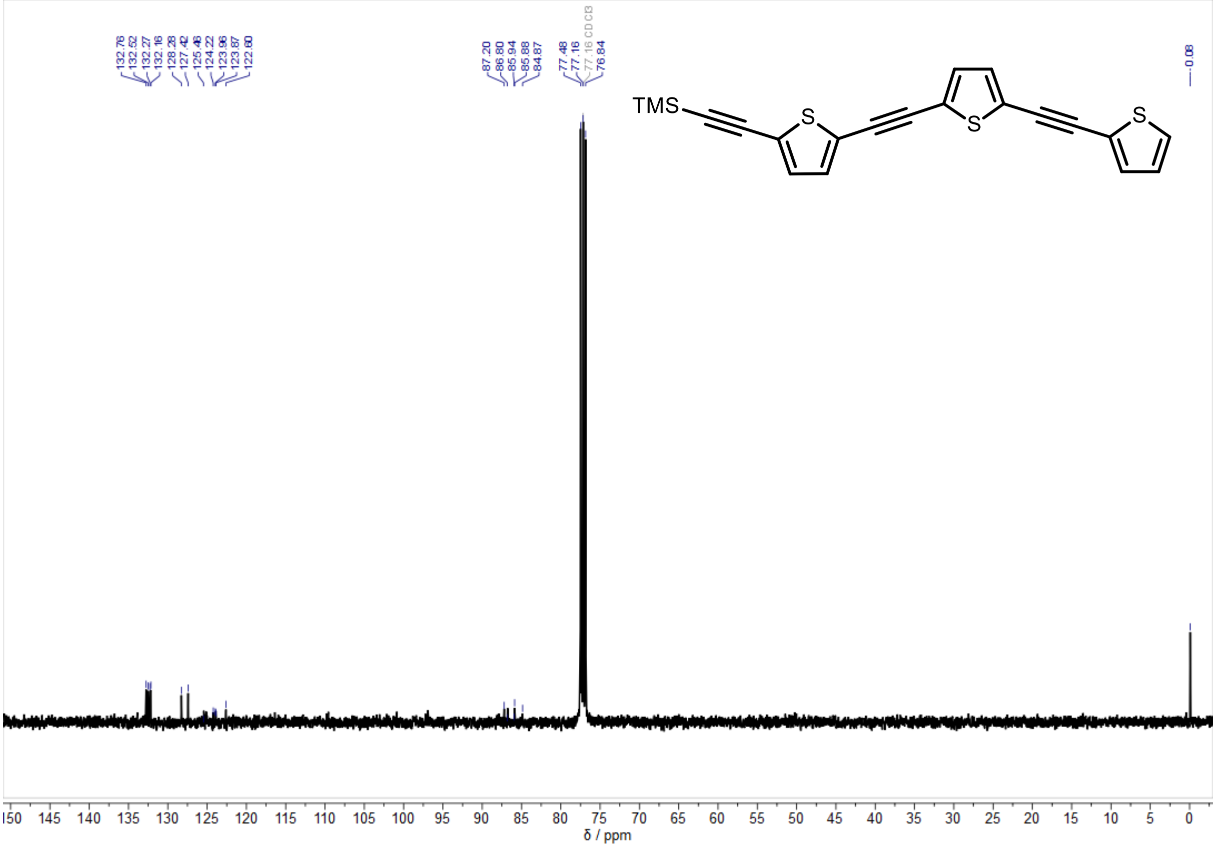
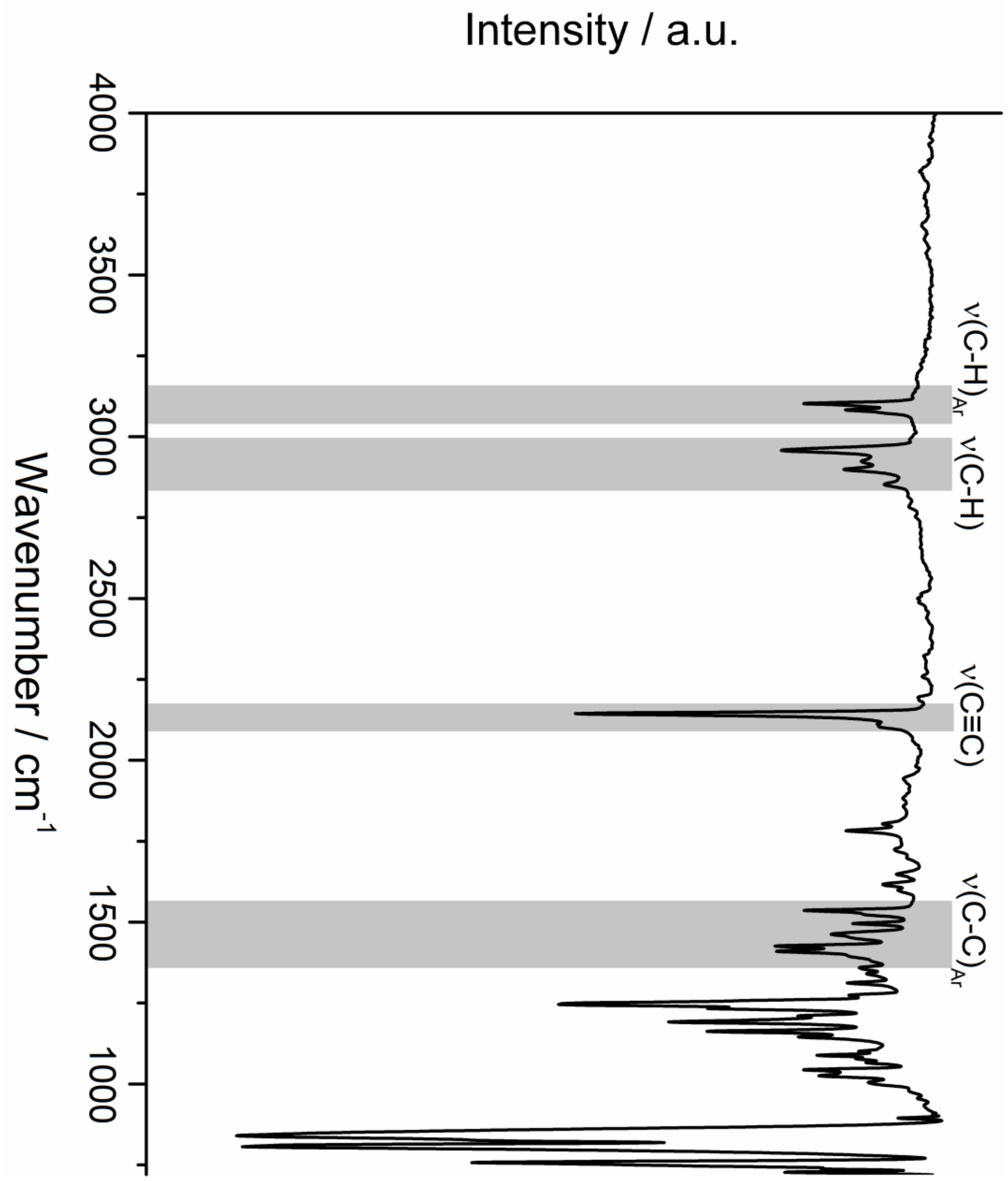
ν(C-H)$_{alkyne}$
ν(C-H)$_{Ar}$
ν(C≡C)
ν(C-C)$_{Ar}$

trimethyl((5-((5-(thiophen-2-ylethynyl)thiophen-2-yl)ethynyl)thiophen-2-yl)ethynyl)silane 12



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ν(C-H)
ν(C≡C)
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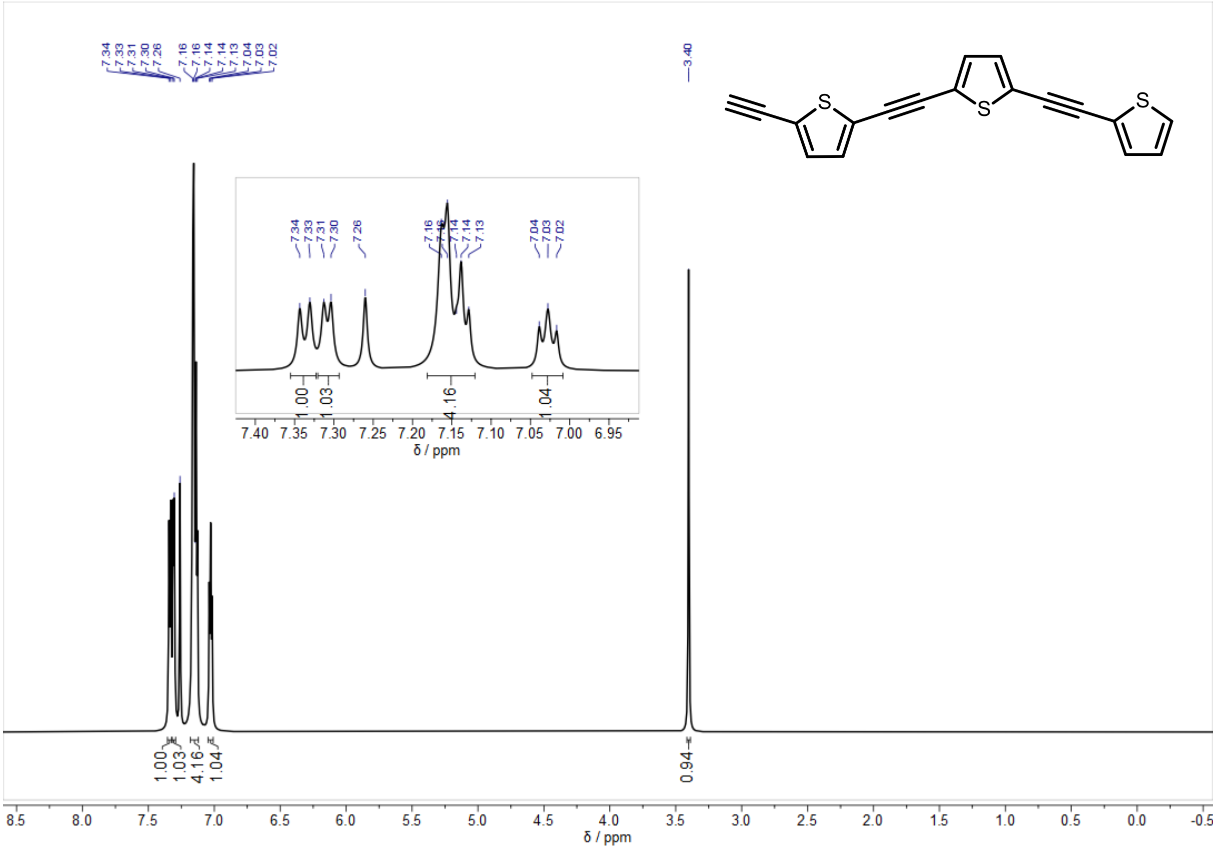
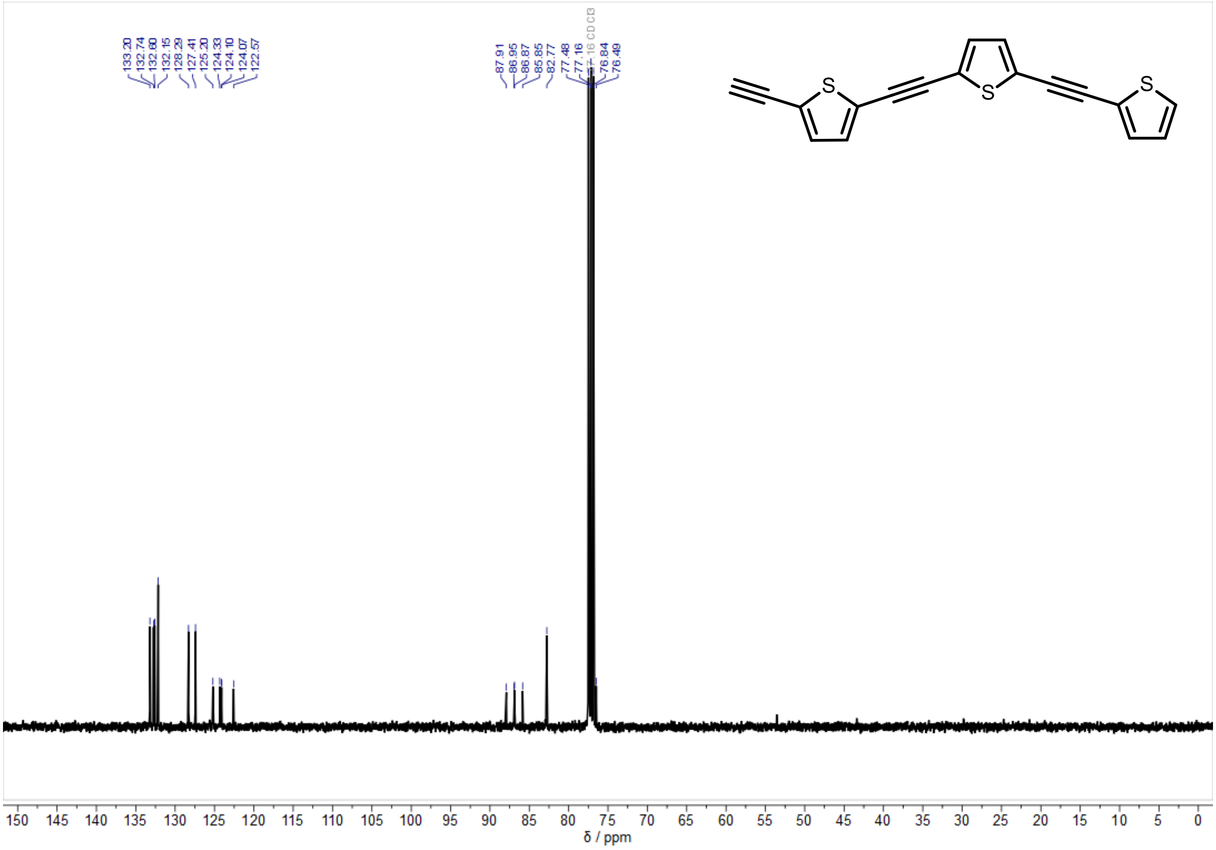
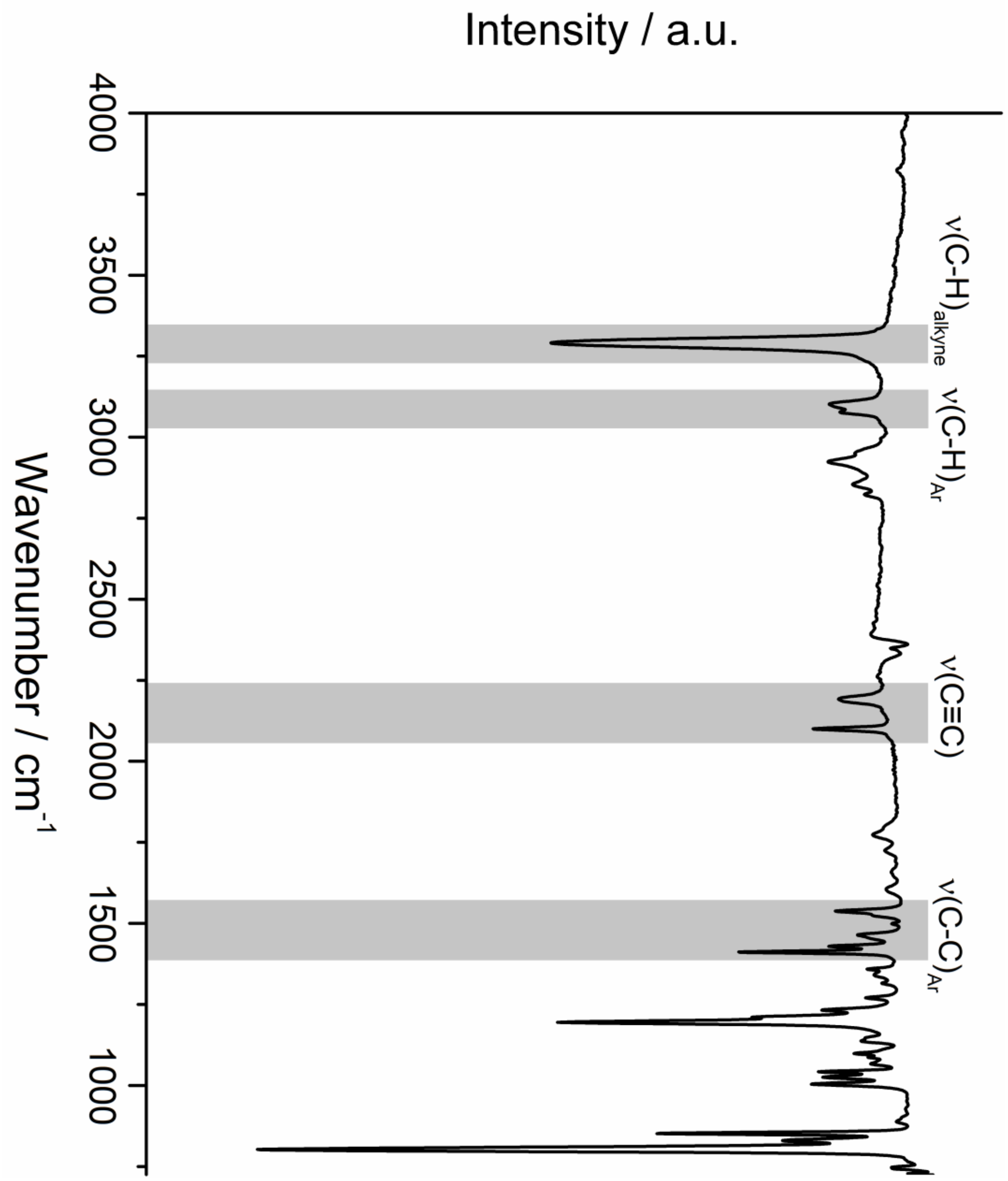
2-ethynyl-5-((5-(thiophen-2-ylethynyl)thiophen-2-yl)ethynyl)thiophene 13



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ν(C-H)$_{Ar}$
ν(C≡C)
ν(C-C)$_{Ar}$

7.3 Preparation of the SiNCs

7.3.1 Preparation of the SiNCs

General information

Unless noted, all commercial reactants and catalysis were purchased from Sigma-Aldrich and used directly without further purification. Dry THF, toluene, and diethyl ether were obtained from an MBraun SPS 800 solvent purification system. Butyllithium was bought as a 2.5 M solution in hexane. FTIR spectra were measured with a Bruker Vertex 70 FTIR using a Platinum ATR from Bruker. Photoluminescence (PL) spectra were taken with an AVA-Spec 2048 from Avantes using a Prizmatix (LED Current controller) as a light source. TGA analysis was performed with a Netzsch TG 209 F1 Libra machine at a heating rate of 10 K/min in an argon flow of 20 mL/min (Ar 4.8) in platinum pans.

	M (g/mol)	Mass (g)	V (ml)	Density	Amount of Substance	Equivalent
H_2SO_4	90.08	320	174.86	1.83	3.55	1.28
Fuming H_2SO_4	90.08	160	86.96	1.84	1.78	0.64
Tol (dry)	92.14		518.67	0.87		0.48
$HSiCl_3$	135.45	250	186.57	1.34	1.85	1
Tol (SPS)	92.14		1000	0.87		4
Tol total			1518.67			
Vol total			1967.06			

Table. 7-1 Synthesis of hydrogen silsesquioxane (HSQ)

Sulfuric acid (175.00 ml) and fuming sulfuric acid were added to a three-necked flask equipped with a stir bar. Dry toluene (519.00 ml) was added via a dropping funnel for 2 hours. After stirring for an additional 30 min, the yellow solution was gained. Toluene (1000 ml), which $HSiCl_3$ (187.00 ml) dissolved in, was added over the above biphasic solution for 4 hours. At a subsequent time, the upper organic phase was separated, washed thrice with sulfuric acid 50 % (w/w), and dried overnight with overdose $MgSO_4$ and $CaCO_3$. A colorless solid was observed after filtration and removing the solvent in *vacuo*.

Preparation of SiNC/SiO_2 Nanocrystals Composite

7 g of HSQ was placed in a quartz reaction boat, then transferred to a quartz working tube in a Nabertherm RD 30/200/11 oven in a slightly reducing gas atmosphere (5% H_2 / 95% N_2). The composite was heated from ambient temperature to a peak temperature of 1100 °C at 18 °C/min. The heating was kept isothermal for an hour. A brownish-black solid was obtained after cooling to room temperature. To enhance a uniform etching of the matrix, the solid was ground to a fine brown powder using a mortar and pestle. The dark powder was disseminated in ethanol and combined with high-purity silicon beads in a WAB Turbula mixer for 24 hours of grinding. The produced mixture was vacuum-dried to generate an earthy yellow powder, which was then stored in a glass vial.

SiNCs/SiO_2 Composite Etching Time Definition

In one polypropylene beaker (equipped with a Teflon-coated stir stirrer), 300 mg of the composite was introduced, followed by 3 mL of water, 3 mL of ethanol, and 3 mL of HF. At three-minute intervals, samples of the dispersion were collected and added to a vial containing a small amount of toluene. IR measurement was performed on the extracted SiNCs/toluene dispersion. The absence of the Si-O stretching band (~1000 cm^{-1}) was used as a criterion for etching time. This step is performed for each composite synthesized.

Liberation of SiNC with HF

Utilizing hydrofluoric acid to etch the SiNCs/SiO_2 complexes, hydride-terminated SiNCs can be obtained. An ethylene-tetrafluoroethylene (ETFE) beaker is prepared with a Teflon-coated stir bar. 300 mg of pre-ground SiNCs/SiO_2 complexes, water (3-mL), and ethanol (3 mL) were added to the beaker, brown suspension was obtained by stirring. Subsequently, hydrofluoric acid (3 mL, 49%) was added and the suspension changed to a deep colour. A yellow suspension was observed after 35 minutes of etching. 5-10 mL of toluene was added to the beaker and the SiNCs in the aqueous phase were extracted into the toluene, which was then transferred to an ETFE-centrifugation tube. The process was repeated twice until the aqueous phase becomes colorless, to ensure that all nanoparticles were extracted. Finally, hydride-terminated SiNCs can be obtained after centrifugation (9000 rpm, 4 mins) and separation.

7.3.2 Preparation of B doped SiNCs

Synthesis of hydrogen silsesquioxane (HSQ) is the same with the above methods (chapter 4.2), the only difference is that HSQ does not need to be dried, and retains as toluene solution. To get the HSQ concentration, 10 mL of a toluene solution of HSQ were dried, and 0.69 g HSQ solid was obtained. In order to mix boric acid and HSQ well, an ethanolic solution of boric acid was obtained with a concentration of 1.0-g per 30 mL. The prepared H_3BO_3 (in EtOH) is added to the HSQ (in Toluene). Four different doping concentrations were ued to investigate the effect of boron-doped nanoparticles on the properties of polymer films.

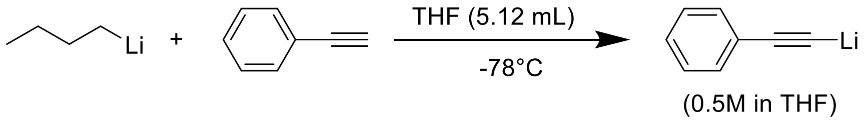
7.4 Functionalization of the SiNCs

7.4.1 One-Step Functionalization of the SiNCs

Synthesis of Organometallic Reagents

To a Schlenk flask equipped with a stir bar, conjugated systems with alkynyl end groups and degassed THF were added. N-butyllithium was added dropwise at -78 °C over a period of 20 minutes. After completion of the reaction, the complexes were stirred for another 15 minutes at -78 °C, followed by warming at room temperature for 15 minutes. The final product was stored in a refrigerator.

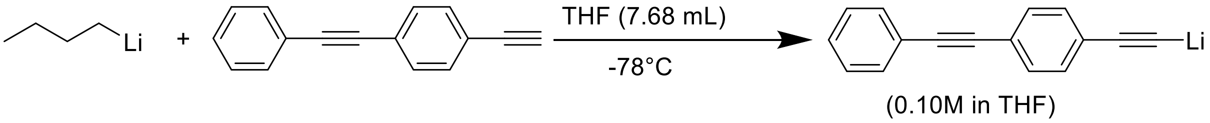
Lithium Phenylacetylide



Reactants *Products*

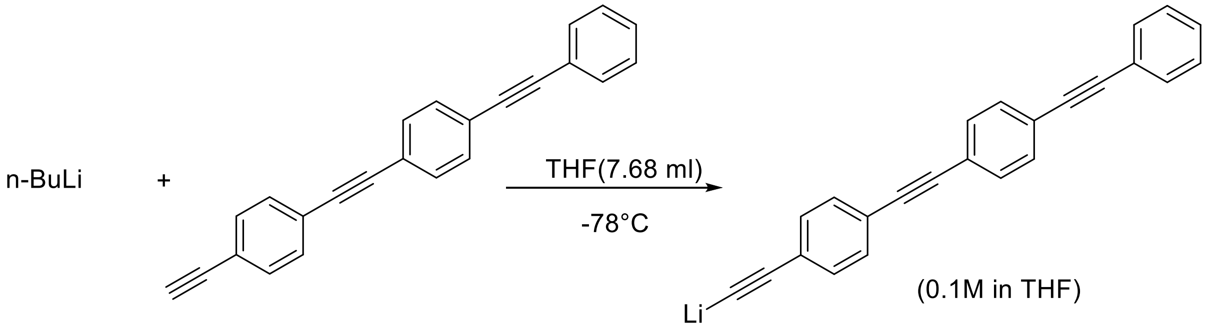
Formula	**C_4H_9Li**	**C_8H_6**	Formula	**C_8H_5Li**
MW	64.06	102.14	MW	108.07
Limiting?	***Yes***	No	Equivalents	
Equivalents	***0.80***		%Completion	
Sample Mass	204.98mg	408.54mg	Expected Mass	432.27mg
%Weight			Expected Moles	4.00mmol
Molarity	***2.50M***		Measured Mass	
Density		***930.00mg/mL***	Purity	
Volume	1.28mL	439.29mmL	Product Mass	
Reactant Moles	***3.20mmol***	4.00mmol	Product Moles	
Reactant Mass	204.98mg	408.54mg	%Yield	

Lithium 1-ethynyl-4-(phenylethynyl)benzene



Reactants			*Products*	
Formula	**C_4H_9Li**	**$C_{16}H_{10}$**	Formula	**$C_{16}H_9Li$**
MW	64.06	202.26	MW	208.19
Limiting?	***Yes***	No	Equivalents	
Equivalents	***0.80***		%Completion	
Sample Mass	51.24mg	202.26mg	Expected Mass	208.19mg
%Weight			Expected Moles	1.00mmol
Molarity	***2.50M***		Measured Mass	
Density			Purity	
Volume	320.00mmL		Product Mass	
Reactant Moles	***800.00µmol***	1.00mmol	Product Moles	
Reactant Mass	51.24mg	202.26mg	%Yield	

Lithium 4-(2-(4-ethynylphenyl)-ethynyl)-1-(2-phenylethynyl)benzene



Reactants			*Products*	
Formula	**C_4H_9Li**	**$C_{24}H_{14}$**	Formula	**$C_{24}H_{13}Li$**
MW	64.06	302.38	MW	308.31
Limiting?	***Yes***	No	Equivalents	
Equivalents	***0.80***	***1.00***	%Completion	
Sample Mass	51.24g	302.38g	Expected Mass	308.31g
%Weight			Expected Moles	1.00mol
Molarity	***2.50M***		Measured Mass	
Density			Purity	
Volume	320.00mL		Product Mass	
Reactant Moles	***800.00mmol***	1.00mol	Product Moles	
Reactant Mass	51.24g	302.38g	%Yield	

Functionalization SiNCs with Organometallic Oeagents

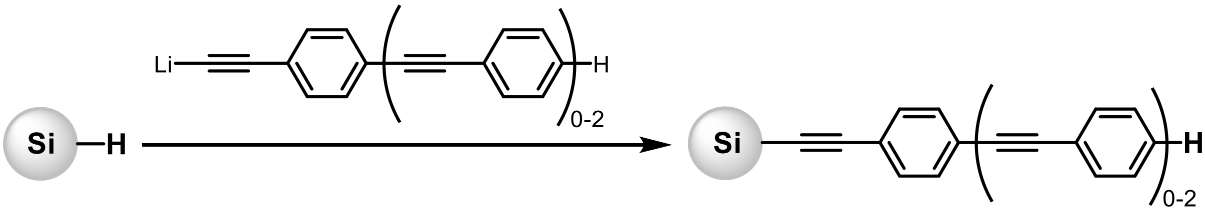
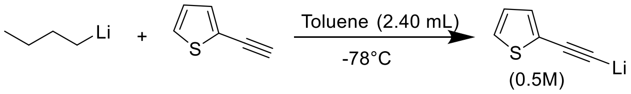


Fig.7-1 Functionalization SiNCs with organometallic reagents.

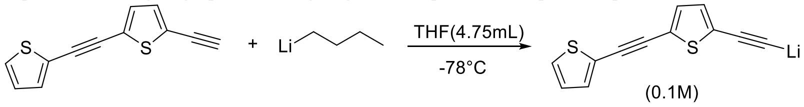
General method: to a Schlenk flask equipped with a stir bar, freshly etched hydride-terminated SiNCs (from 300 mg SiNCs/SiO_2) were dispersed into 2 ml degassed dry toluene. Organometallic reagents (0.2 mmol) were added to the complexes individually, and the yellow suspension changed to brown. The reaction was placed at room temperature and the reaction components were stirred overnight. To a prepared ETFE-centrifugation tube with 5-10 ml (methanol : ethanol = 1 : 1) mixed solvents, the reaction components were transferred to it, and subsequently, hydrochloric acid (HCl conc., 0.2 ml) was added to acidify. Functionalized SiNCs can be obtained after centrifugation (9000 rpm, 4 mins) and separation. 10-15 drops of toluene were added to redisperse the sediment. This precipitation-centrifugation-redispersion step was repeated twice. Finally, the functionalized SiNCs were dispersed into a small amount of toluene for the subsequent characterization.

Lithium ethynylthiophene (ET-1)



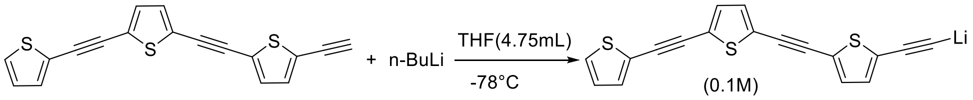
Reactants			*Products*	
Formula	**C_4H_9Li**	**C_6H_4S**	Formula	**C_6H_3LiS**
MW	64.06	108.16	MW	114.09
Limiting?	***Yes***	No	Equivalents	
Equivalents	***1.00***	***0.80***	%Completion	
Sample Mass	128.11 mg	173.05mg	Expected Mass	228.18mg
%Weight			Expected Moles	2.00mmol
Molarity	***2.50M***		Measured Mass	
Density		***1.14g/mL***	Purity	
Volume	800.00mmL	151.80mmL	Product Mass	
Reactant Moles	***2.00mmol***	1.60mmol	Product Moles	
Reactant Mass	128.11 mg	173.05mg	%Yield	

Lithium 1-(thiophenethynyl)-4-ethynylthiophene (ET-2)



Reactants			Products	
Formula	**$C_{12}H_6S_2$**	**C_4H_9Li**	Formula	**$C_{12}H_5LiS_2$**
MW	214.30	64.06	MW	220.23
Limiting?	***Yes***	No	Equivalents	
Equivalents	***0.80***	***1.00***	%Completion	
Sample Mass	107.15mg	40.04mg	Expected Mass	137.65mg
%Weight			Expected Moles	625.00µmol
Molarity		***2.50M***	Measured Mass	
Density			Purity	
Volume		250.00mmL	Product Mass	
Reactant Moles	***500.00µmol***	625.00µmol	Product Moles	
Reactant Mass	107.15mg	40.04mg	%Yield	

Lithium 4-(2-(4-ethynylphenyl)-ethynyl)-1-(2-phenylethynyl)benzene (ET-3)



Reactants			Products	
Formula	**$C_{18}H_8S_3$**	**C_4H_9Li**	Formula	**$C_{18}H_7LiS_3$**
MW	320.44	64.06	MW	326.37
Limiting?	***Yes***	No	Equivalents	
Equivalents	***0.80***	***1.00***	%Completion	
Sample Mass		40.04mg	Expected Mass	203.98mg
%Weight			Expected Moles	625.00µmol
Molarity		***2.50M***	Measured Mass	
Density			Purity	
Volume		250.00mmL	Product Mass	
Reactant Moles	***500.00µmol***	625.00µmol	Product Moles	
Reactant Mass	160.22mg	40.04mg	%Yield	

Functionalization of SiNCs with organometallic reagents

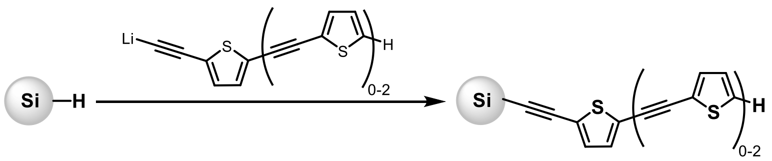


Fig.7-2 Functionalization of SiNCs with organometallic reagents

General method: To a Schlenk flask equipped with a stir bar, freshly etched hydride-terminated SiNCs (from 300 mg SiNCs/SiO_2) were dispersed into 2 mL degassed dry toluene. Organometallic reagents (0.2 mmol) were added to the Schlenk flask at room temperature, upon this addition the yellow suspension changed to brown. The reaction mixture was stirred overnight at room temperature. The reaction mixture was transferred into an ETFE-centrifugation tube filled with 5 to 10 mL methanol/ethanol mixture (1:1) and subsequently quenched with 0.2 mL conc. hydrochloric acid. Functionalized SiNCs were obtained after centrifugation (9000 rpm, 4 minutes) and separation. 10-15 drops of toluene were added to redisperse the sediment. This precipitation-centrifugation-redispersion step was repeated twice. Finally, the functionalized SiNCs were dispersed into a small amount of toluene for the subsequent characterization via FTIR and PL spectroscopy. Samples for TGA were freeze-dried from benzene.

Functionalization SiNCs with 1-dodecene

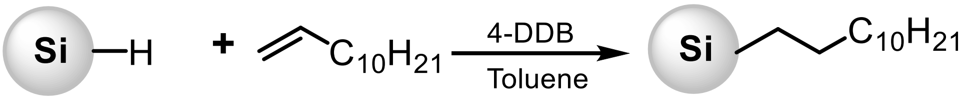


Fig.7-3 Functionalization SiNCs with 1-dodecene.

To a Schlenk flask equipped with a stir bar, freshly etched hydride-terminated SiNCs (from 300 mg SiNCs/SiO_2) were dispersed into 2 ml degassed dry toluene. 1-dodecene (2 mmol, 0.44 ml) and 4-decylbenzene diazonium tetrafluoroborate (5-6 mg) were added to the complexes. The reaction was placed at room temperature and the reaction components were stirred overnight. To a prepared ETFE-centrifugation tube with 5-10 ml (methanol : ethanol = 1 : 1) mixed solvents, the reaction components were transferred to it. Functionalized SiNCs can be obtained after centrifugation (9000 rpm, 4 mins) and separation. 10-15 drops of toluene were added to redisperse the sediment. This precipitation-centrifugation-redispersion step was repeated twice. Finally, the functionalized SiNCs were dispersed into a small amount of toluene for the subsequent characterization.

7.3.3 Two-Steps Functionalization of the SiNCs

Synthesis of hydrogen silsesquioxane (HSQ), preparation of SiNC/SiO_2 nanocrystals composite, and SiNC/SiO_2 composite etching time definition are the same as One-step functionalization methods (chapter 7.2.1).

Liberation of SiNC with HF

In order to compare the difference in PL value, SiNCs are etched by the same step. An ethylene-tetrafluoroethylene (ETFE) beaker is prepared with a Teflon-coated stir bar. 600 mg of pre-ground SiNCs/SiO_2 complexes, water (6 mL), and ethanol (6-mL) were added to the beaker, brown suspension was obtained by stirring. Subsequently, hydrofluoric acid (6 mL, 49%) was added and the suspension changed to a deep color. A yellow suspension was observed after 35 minutes of etching. 5-10 mL of toluene was added to the beaker and the SiNCs in the aqueous phase were extracted into the toluene, which was then transferred to an ETFE-centrifugation tube. The process was repeated twice until the aqueous phase becomes colorless, to ensure that all nanoparticles were extracted. Finally, hydride-terminated SiNCs can be obtained after centrifugation (9000 rpm, 4 minutes) and separation.

Functionalization SiNCs with Organometallic Reagents

General method: to a Schlenk flask equipped with a stir bar, freshly etched hydride-terminated SiNCs (from 600 mg SiNCs/SiO_2) were dispersed into 4 mL degassed dry toluene. Organometallic reagents (0.4 mmol) were added to the complexes individually, and the yellow suspension changed to brown. The reaction was placed at room temperature and the reaction components were stirred overnight. To a prepared ETFE-centrifugation tube with 5-10 mL (methanol : ethanol = 1 : 1) mixed solvents, the reaction components were transferred to it, and subsequently, hydrochloric acid (HCl conc., 0.4 mL) was added to acidify. Functionalized SiNCs can be obtained after centrifugation (9000 rpm, 4 minutes) and separation. 15-20 drops of toluene were added to redisperse the sediment. This precipitation-centrifugation-redispersion step was repeated twice. Finally, the functionalized SiNCs were dispersed into 3 mL of dry toluene for the subsequent characterization.

The Second SiNCs Functionalization Steps with 1-dodecene

To a Schlenk flask equipped with a stir bar, the above SiNCs and toluene mixture (2 mL) was transferred. The mixture was degassed three times to get an oxygen-free system with freeze-pump-thaw. 1-dodecene (2 mmol, 0.44 mL) and 4-decylbenzene diazonium tetrafluoroborate (5-6 mg) were added to the complexes. The reaction was placed at room temperature and the reaction components were stirred overnight. To a prepared ETFE-centrifugation tube with 5-10 mL (methanol : ethanol = 1 : 1) mixed solvents, the reaction components were transferred to it. Functionalized SiNCs can be obtained after centrifugation (9000 rpm, 4 minutes) and separation. 10-15 drops of toluene were added to redisperse the sediment. This precipitation-centrifugation-redispersion step was repeated twice. Finally, the functionalized SiNCs were dispersed into a small amount of toluene for the subsequent characterization.

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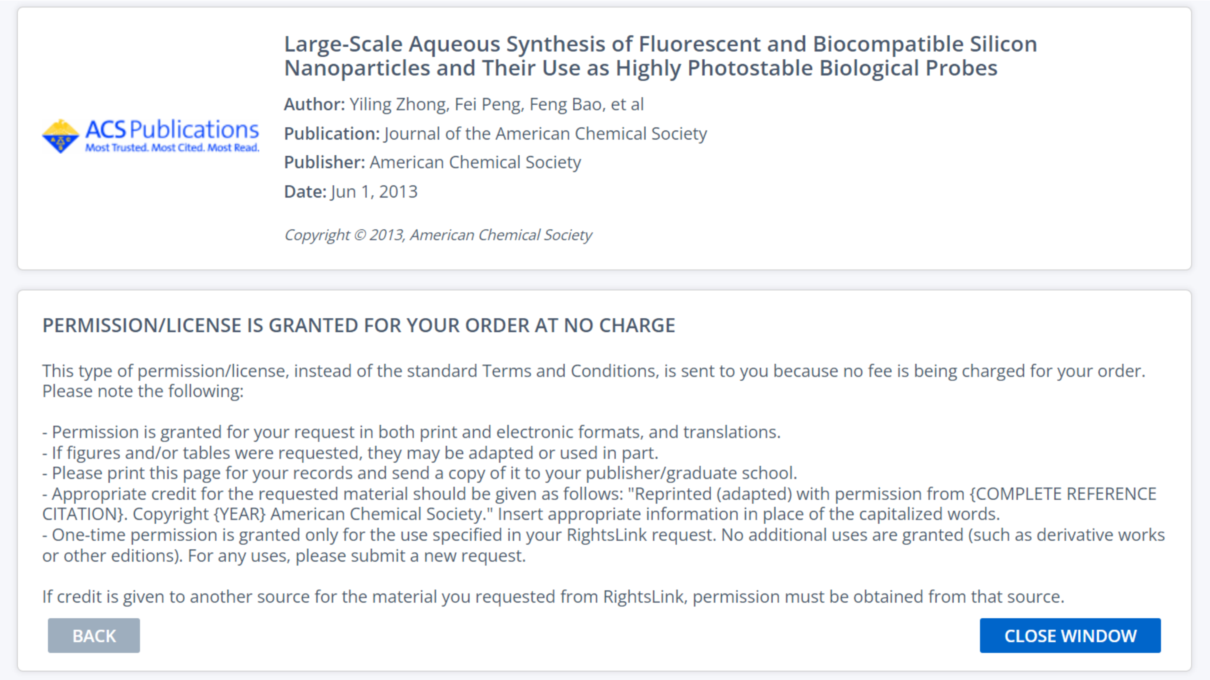

Large-Scale Aqueous Synthesis of Fluorescent and Biocompatible Silicon Nanoparticles and Their Use as Highly Photostable Biological Probes

Author: Yiling Zhong, Fei Peng, Feng Bao, et al

Publication: Journal of the American Chemical Society

Publisher: American Chemical Society

Date: Jun 1, 2013

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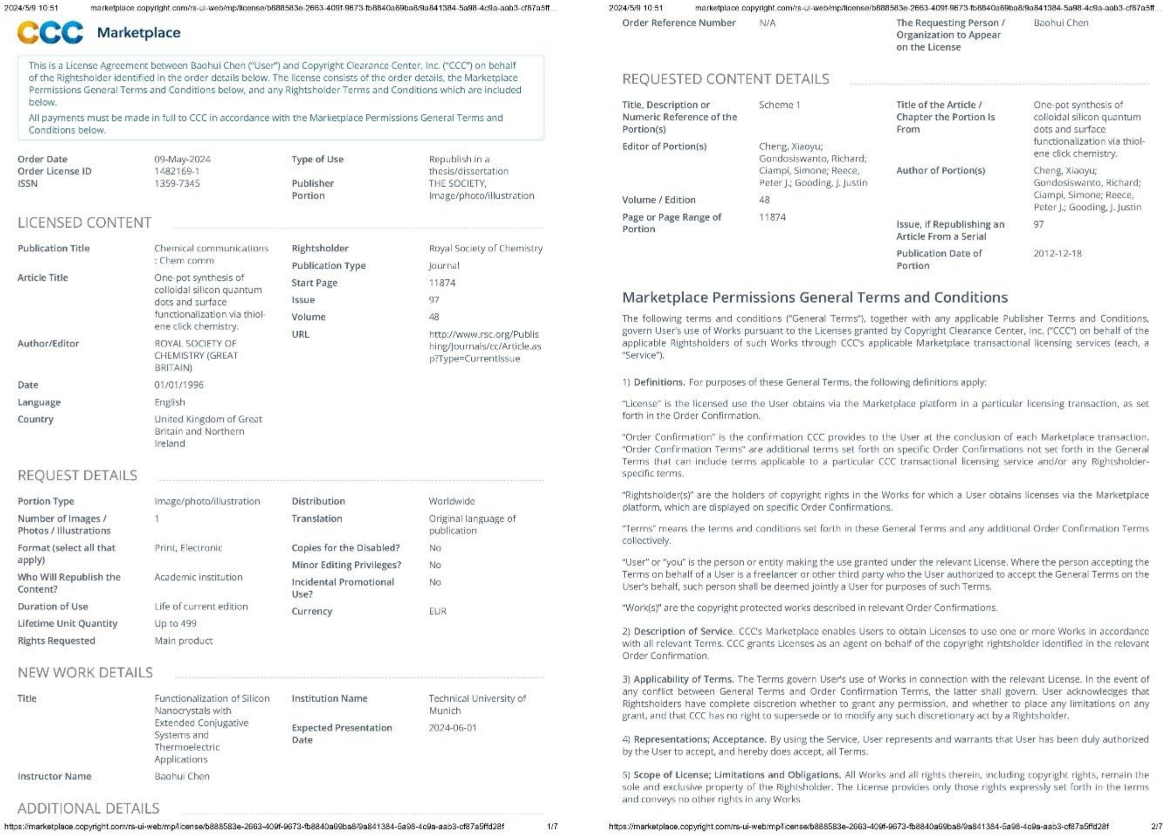

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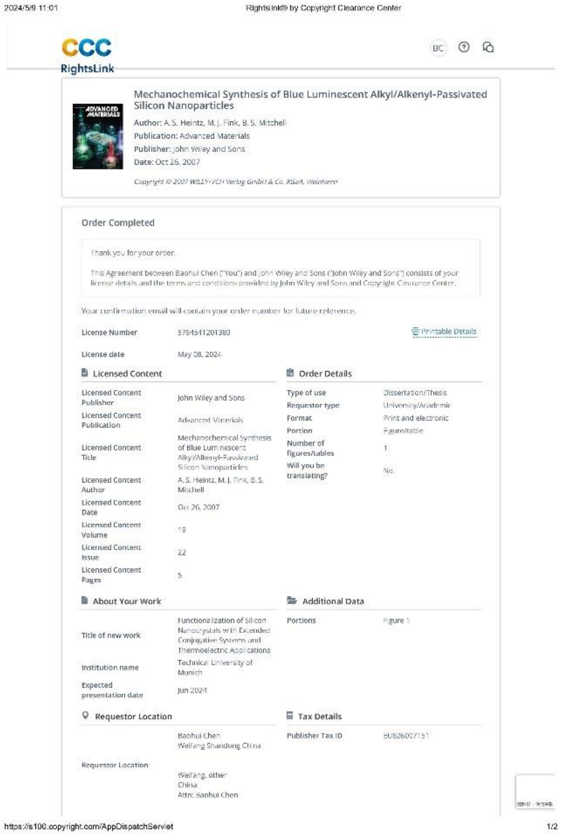

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Mechanochemical Synthesis of Blue Luminescent Alkyl/Alkenyl-Passivated Silicon Nanoparticles

Author: A. S. Heintz, M. J. Fink, B. S. Mitchell
Publication: Advanced Materials
Publisher: John Wiley and Sons
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Simple Preparation of Fluorescent Silicon Nanoparticles from Used Si Wafers

Author: Jangsun Hwang, Yoon Jeong, Kwan Hong Lee, et al

Publication: Industrial & Engineering Chemistry Research

Publisher: American Chemical Society

Date: Jun 1, 2015

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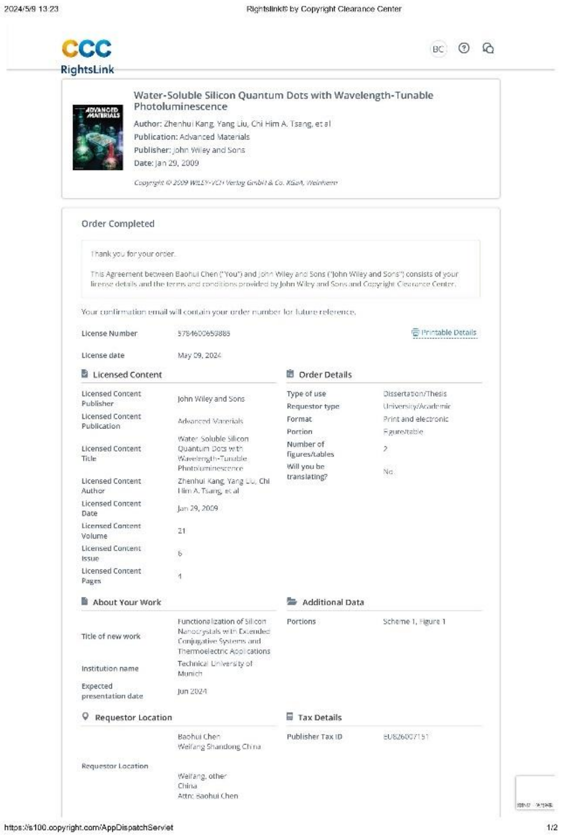

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Water-Soluble Silicon Quantum Dots with Wavelength-Tunable Photoluminescence

Author: Zhenhui Kang, Yang Liu, Chi Him A. Tsang, et al

Publication: Advanced Materials

Publisher: John Wiley and Sons

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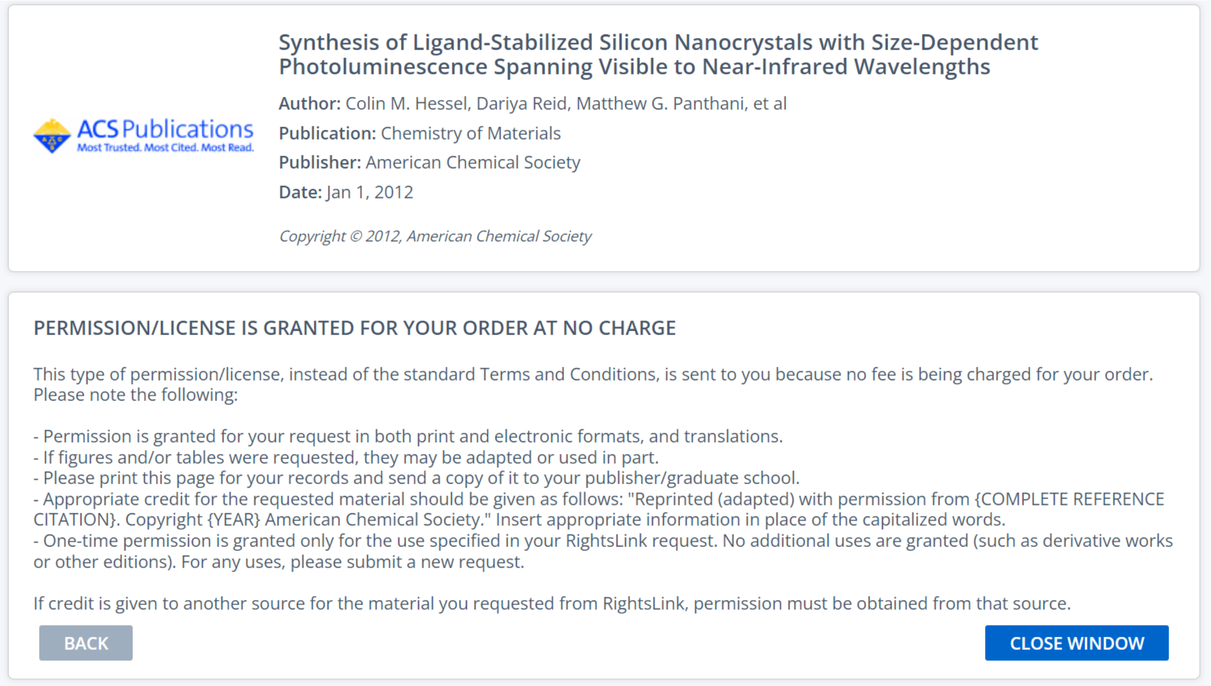

Synthesis of Ligand-Stabilized Silicon Nanocrystals with Size-Dependent Photoluminescence Spanning Visible to Near-Infrared Wavelengths

Author: Colin M. Hessel, Dariya Reid, Matthew G. Panthani, et al
Publication: Chemistry of Materials
Publisher: American Chemical Society
Date: Jan 1, 2012

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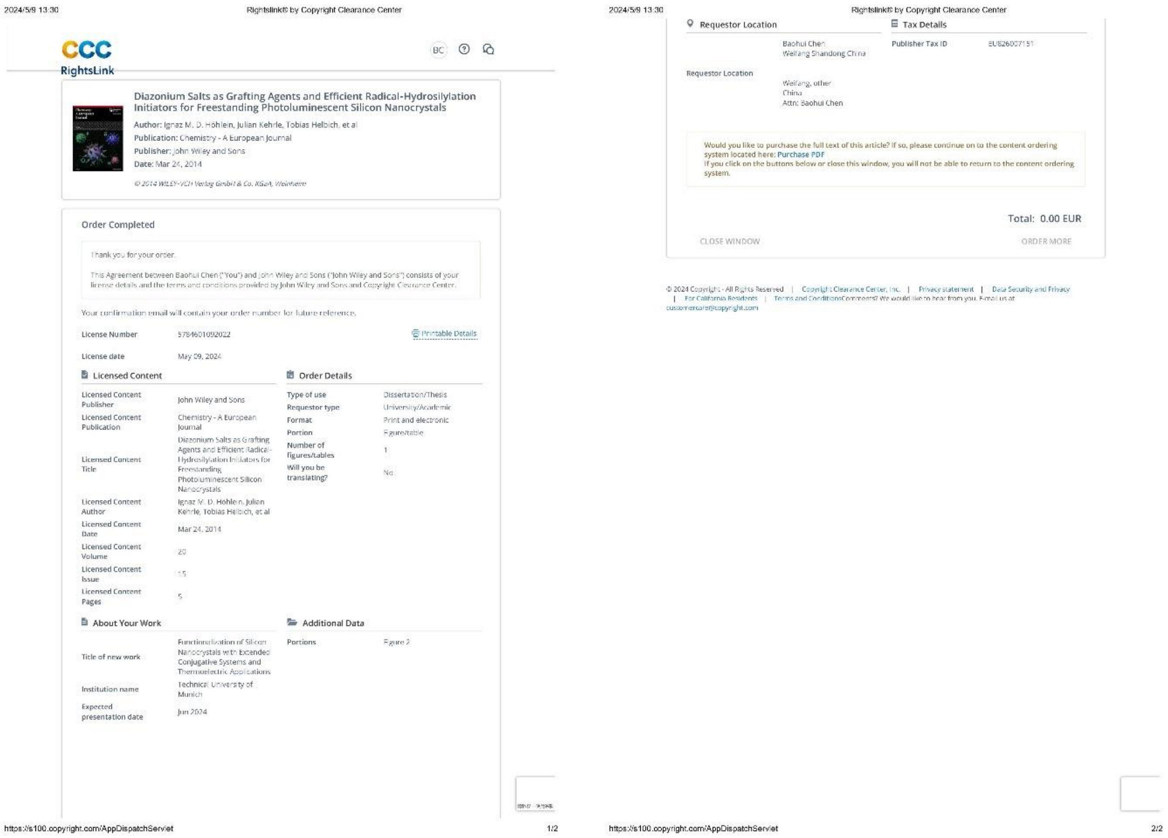

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Author: Ignaz M. D. Höhlein, Julian Kehrle, Tobias Helbich, et al
Publication: Chemistry - A European Journal
Publisher: John Wiley and Sons
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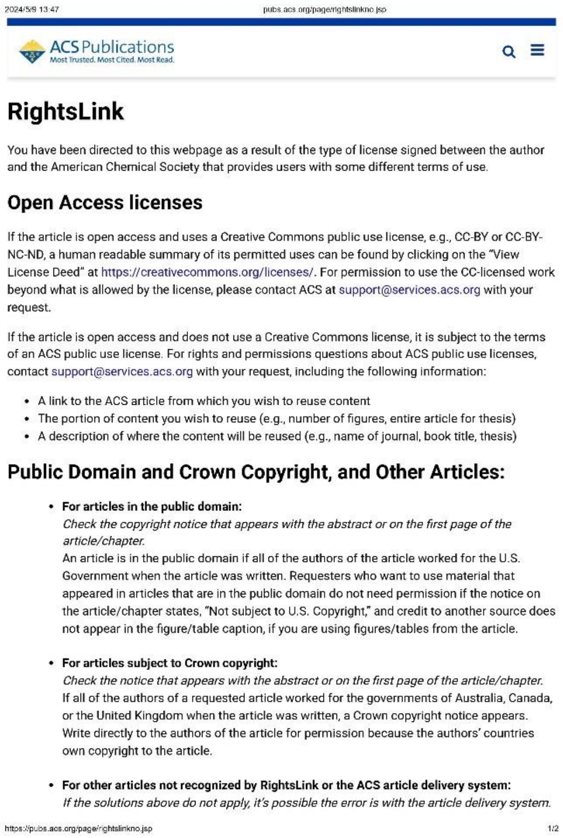

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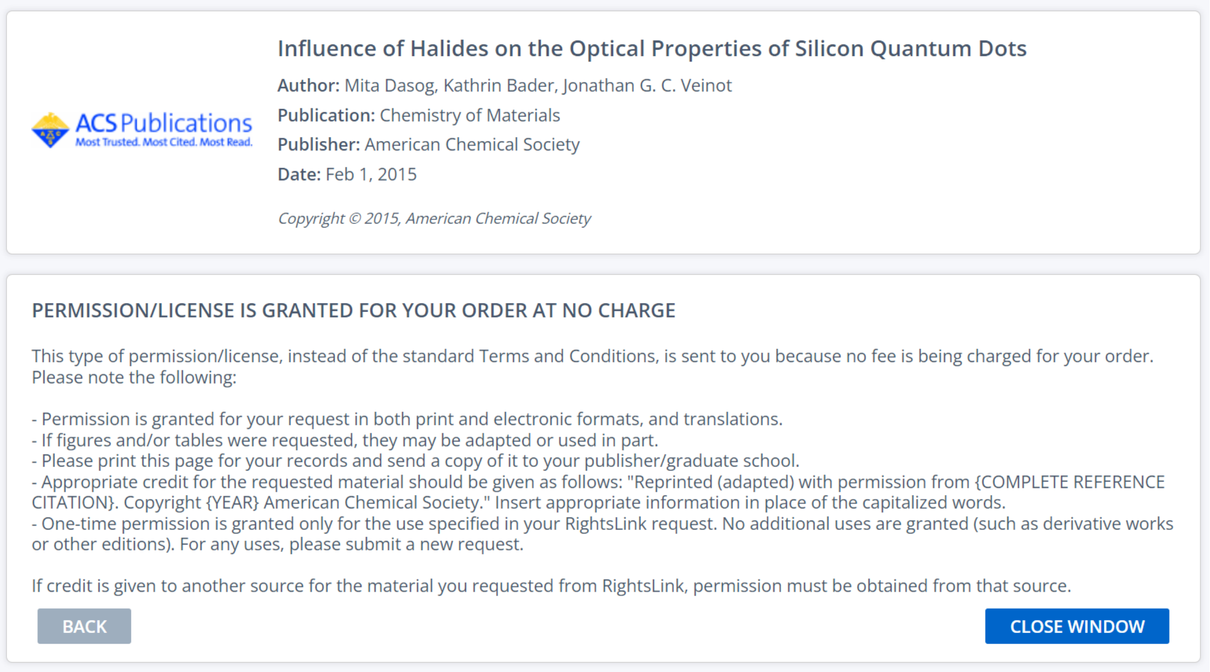

Influence of Halides on the Optical Properties of Silicon Quantum Dots

Author: Mita Dasog, Kathrin Bader, Jonathan G. C. Veinot
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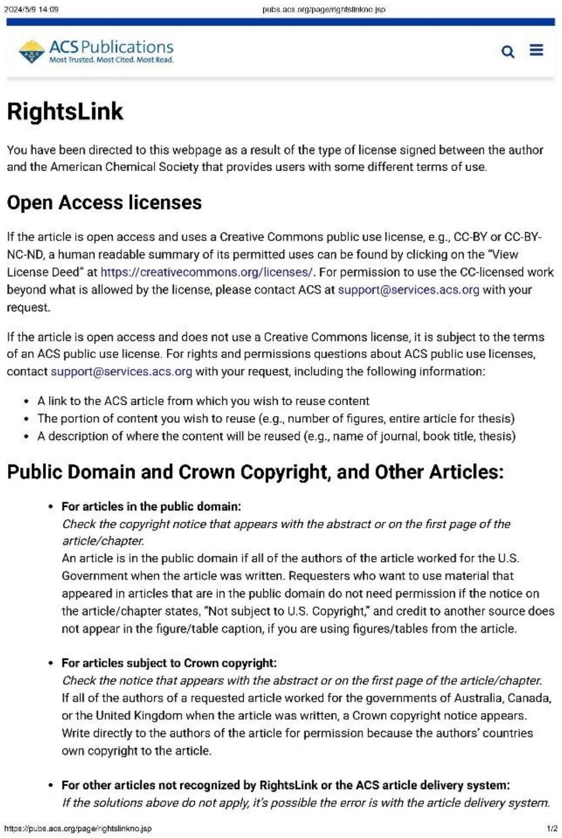

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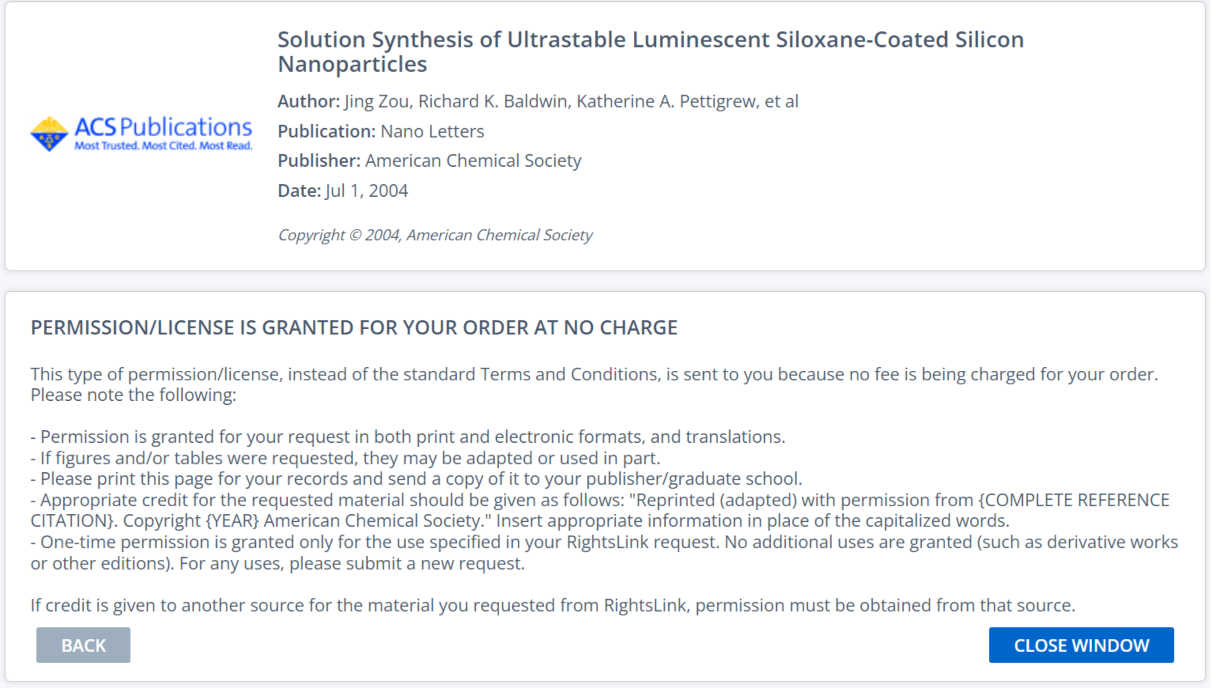

Solution Synthesis of Ultrastable Luminescent Siloxane-Coated Silicon Nanoparticles

Author: Jing Zou, Richard K. Baldwin, Katherine A. Pettigrew, et al

Publication: Nano Letters

Publisher: American Chemical Society

Date: Jul 1, 2004

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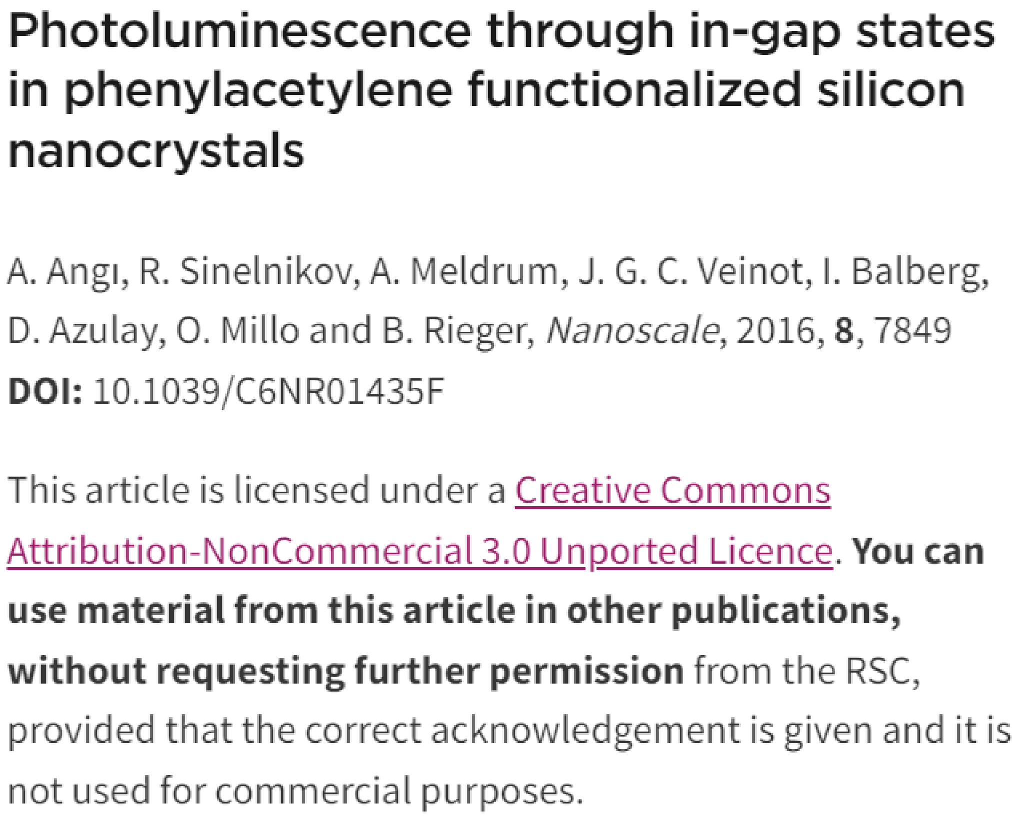

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A. Angı, R. Sinelnikov, A. Meldrum, J. G. C. Veinot, I. Balberg, D. Azulay, O. Millo and B. Rieger, *Nanoscale*, 2016, **8**, 7849

DOI: 10.1039/C6NR01435F

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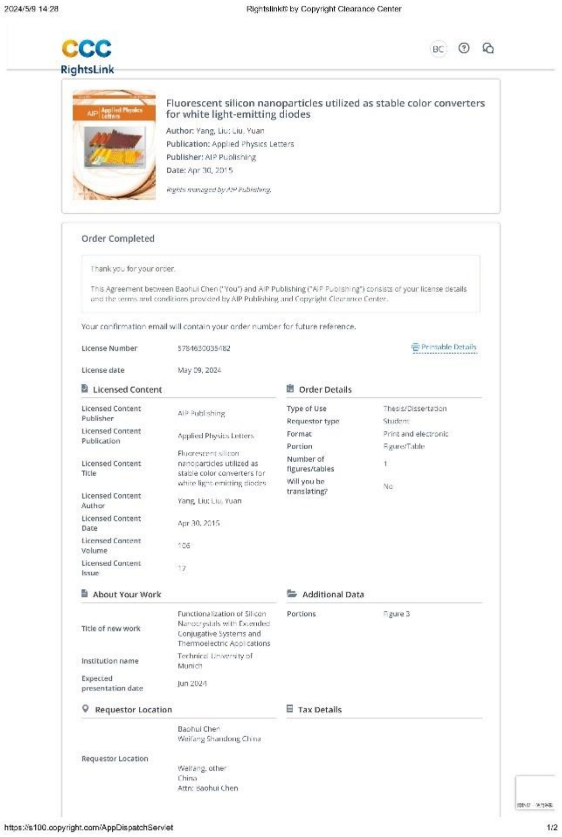

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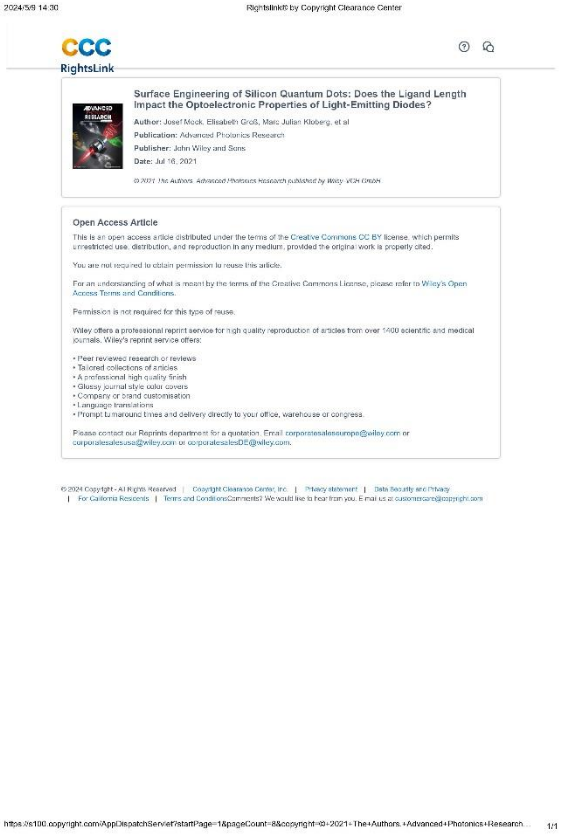

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Surface Engineering of Silicon Quantum Dots: Does the Ligand Length Impact the Optoelectronic Properties of Light-Emitting Diodes?

Author: Josef Mock, Elisabeth Groß, Marc Julian Kloberg, et al

Publication: Advanced Photonics Research

Publisher: John Wiley and Sons

Date: Jul 16, 2021

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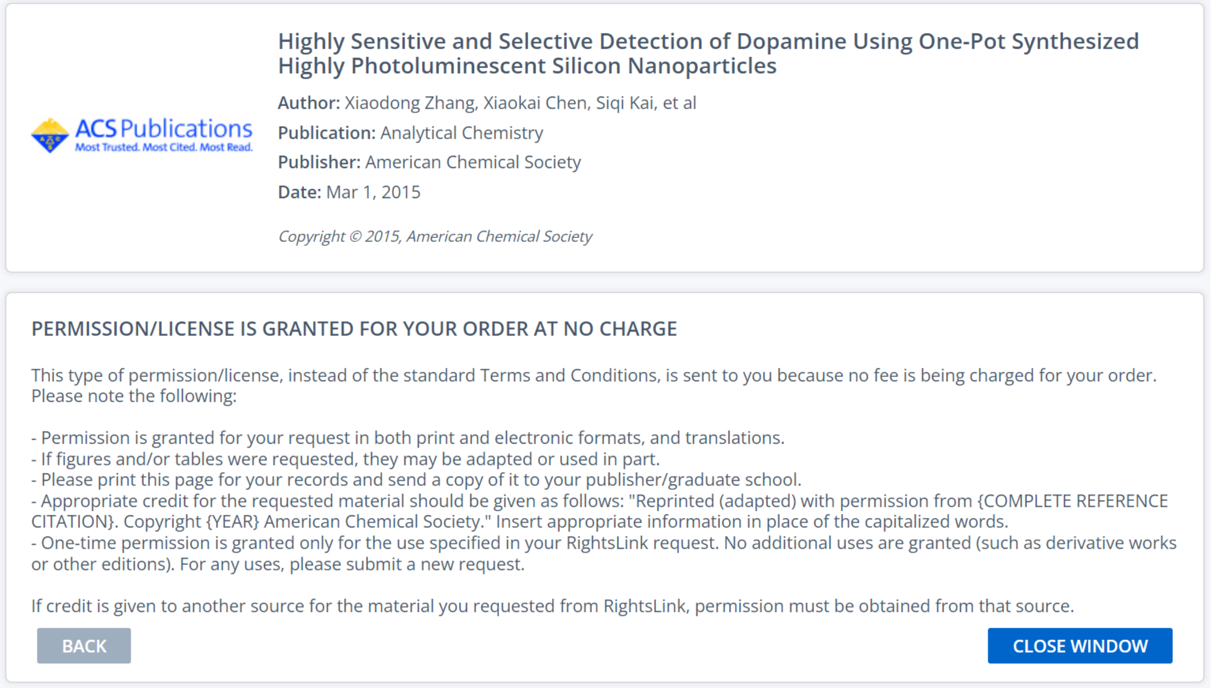

Highly Sensitive and Selective Detection of Dopamine Using One-Pot Synthesized Highly Photoluminescent Silicon Nanoparticles

Author: Xiaodong Zhang, Xiaokai Chen, Siqi Kai, et al

Publication: Analytical Chemistry

Publisher: American Chemical Society

Date: Mar 1, 2015

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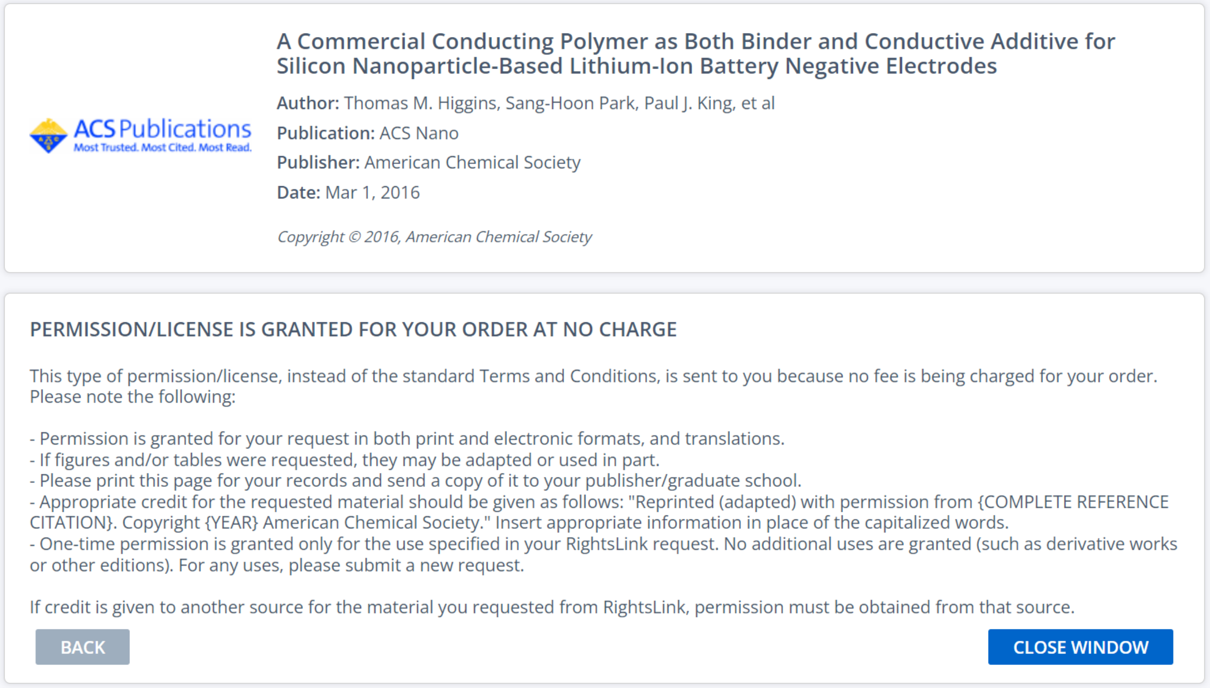

A Commercial Conducting Polymer as Both Binder and Conductive Additive for Silicon Nanoparticle-Based Lithium-Ion Battery Negative Electrodes

Author: Thomas M. Higgins, Sang-Hoon Park, Paul J. King, et al
Publication: ACS Nano
Publisher: American Chemical Society
Date: Mar 1, 2016

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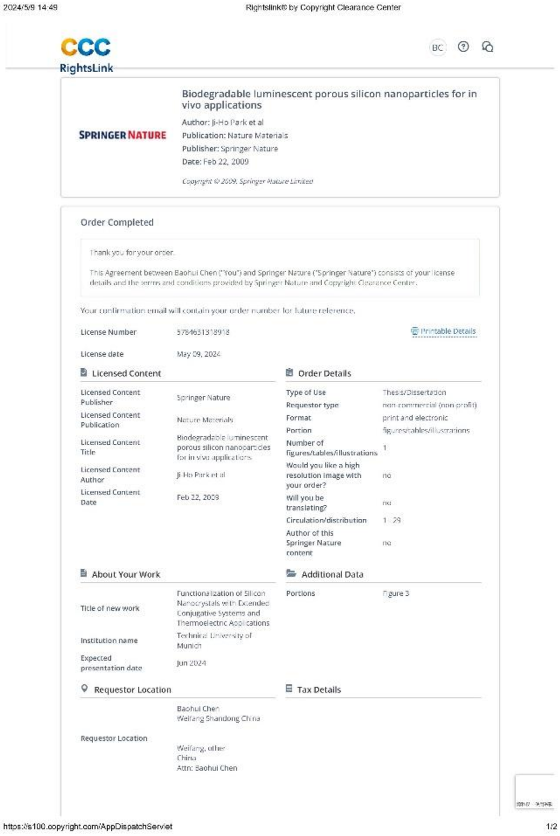

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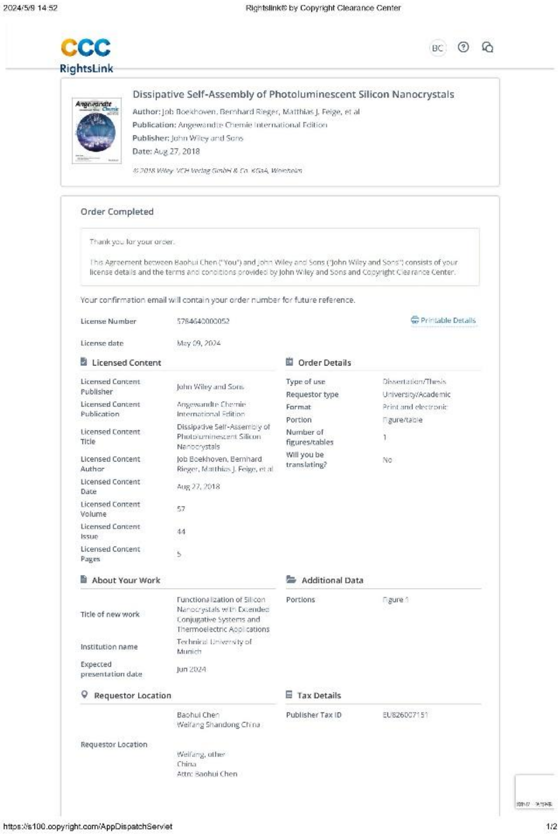

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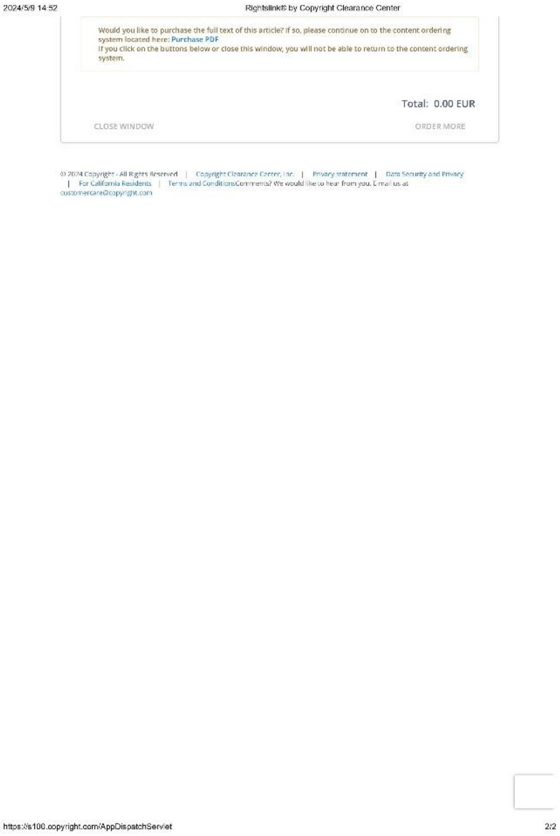

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