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Synthesis of hydrogen- and methyl-capped long-chain polyynes by intense ultrashort laser pulse irradiation of toluene

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ABSTRACT

Hydrogen- and methyl-capped polyynes have been synthesized by irradiating pure liquid toluene with 35 fs, 300 μJ laser pulses having a central wavelength of 800 nm, generated by a regeneratively amplified Ti:sapphire tabletop laser at a repetition rate of 1 kHz. Raman spectroscopy was used to confirm the presence of polyynes in the irradiated samples while high-performance liquid chromatography was used to separate hydrogen-capped polyynes up to $C_{18}H_2$ and methyl-capped polyynes up to $HC_{14}CH_3$. These represent the first such methyl-capped polyynes and the longest hydrogen capped chains synthesized to date by the ultrafast laser based method. Furthermore our results show that choice of the starting solvent molecule directly influences the end caps of the polyynes which can be produced.

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1. Introduction

Polyynes are molecules consisting entirely of sp-hybridized carbon bonds with chemical formula $(-C\equiv C-)_n$ where $n > 1$. They may be capped on either end, by hydrogen or larger end groups, which serve to stabilize longer chains [1], modify electronic and optical properties [2], or grant exotic properties [3]. Polyynes may possibly be used as nano-conductors as they can form novel coaxial nano-wires by insertion into single wall carbon nanotubes [4] and have also been observed in nanostructured thin films [5]. Carbyne, a theoretical allotrope of carbon consisting of infinite polyyne chains, has been predicted to be stable at room temperature with a specific strength twice that of graphene. With appropriate CH_2 end caps the carbon chain may be endowed with nonzero tensile stiffness and with a further 90° twist it may also switch into a magnetic semiconductor state [3].

While the traditional method used to synthesize polyynes, oxidative coupling, has recently been used to generate long chain polyynes ($n = 22$) with stabilizing endcaps [1], the synthesis of carbyne has yet to be realized. Of particular note is that organic synthesis has also been successful for producing macroscopic quantities of cyanopolyynes such as HC_5N [6]. Oxidative coupling itself remains a challenging, multistep procedure that can be extremely hazardous [7]. Recent progress on synthesizing carbyne has involved the growth of linear carbon chains in carbon nanotubes. Shi et al. [8] were able to synthesize polyynes thousands of carbon atoms long by using high vacuum alcohol chemical vapor deposition to synthesize double-walled carbon nanotubes then using high temperature high vacuum annealing to grow the linear carbon chains inside them. Kang et al. [2] synthesized linear carbon chains in multi-walled carbon nanotubes using atmospheric arc discharge in the presence of boron. However, the growth mechanisms employed are not fully understood yet and so it is unclear as to how the end caps may be modified. Recently, two methods involving pulsed laser irradiation have been successfully used to produce polyynes. The first involves the nanosecond laser irradiation of suspended carbon particles (e.g. graphite, fullerenes, and nano-diamond) in organic solvents [9] producing polyynes up to

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$C_{30}H_2$ in certain experiments [10]. In the second and more facile method, femtosecond laser radiation directly initiates synthesis through irradiation of an organic liquid without the need for the introduction of any carbon particles [11]. Sato et al. [12] have used this method to irradiate hexane, producing polyynes up to $C_{12}H_2$, and Wesolowski et al. [13] irradiated benzene, producing both amorphous carbon nanoparticles and polyynes up to $C_{14}H_2$; however, all synthesized polyynes were hydrogen-capped.

As the number of carbon atoms and the end caps can modify the electronic and optical properties of polyynes [2,3], the ability to control the chemical structure of the end caps is desirable. To date, this has not been demonstrated using laser based synthesis methods. To determine if the chemical structure of polyyne end caps can be influenced in laser based synthesis experiments and thereby expand on the potential utility of these polyyne synthesis techniques we have irradiated toluene (methylbenzene) with the aim of creating methyl-capped polyynes.

2. Experimental

High-performance liquid chromatography (HPLC) grade toluene (Sigma Aldrich CHROMASOLV®, ≥99.9% purity) in small glass vials (4.7 mL, base of 15 × 15 mm, height of 45 mm) was irradiated using 35 fs, 300 μJ laser pulses from a regeneratively amplified Ti:Sapphire tabletop laser with a 1 kHz repetition rate and central wavelength of 800 nm. Typically 1–1.5 mL of toluene was used. A schematic of this setup is shown in Fig. 1(a).

The laser beam was focused at the meniscus of the liquid using a mirror and a 50 mm focal length biconvex lens as shown in Fig. 1(a). Consequently, a very intense (> 10^{13} W/cm^2), highly luminous, dissociation and ionization region formed intersecting the air-liquid boundary, visible in Fig. 1(b1) and 1(b2). Within a half hour after the start of the irradiation, the toluene formed a slight yellow hue, which continually darkened as the irradiation progressed. By the 90-min mark, a black precipitate began to form on the liquid meniscus starting at the walls and after 3 h of irradiation covered most of the liquid surface. Physically disturbing the vial caused the precipitate to break up into macroscopic carbon particles that were free to move in the liquid due to the turbulence and convection caused by the energy released in the laser focus. The irradiation time was varied between 1 and 4 h in 1 h steps, however, sufficient polyyne concentrations were found only in the 3 and 4-h samples. Photographs of the irradiated samples are shown in Fig. 1(c).

Irradiated samples were then characterized by Raman spectroscopy and high-performance liquid chromatography (HPLC). Raman spectroscopic measurements were carried out on a Renishaw micro-Raman Spectrometer with an objective magnification of 50 and an excitation wavelength of 488 nm (0.5 mW). For HPLC, a Shimadzu LC-10A liquid chromatographic system equipped with a photodiode array detector (PDA) for UV absorption was used. 100 μL of the irradiated toluene solution was injected into a Wakosil 5C18AR polymeric octadecyl silica (ODS) column and eluted by *n*-

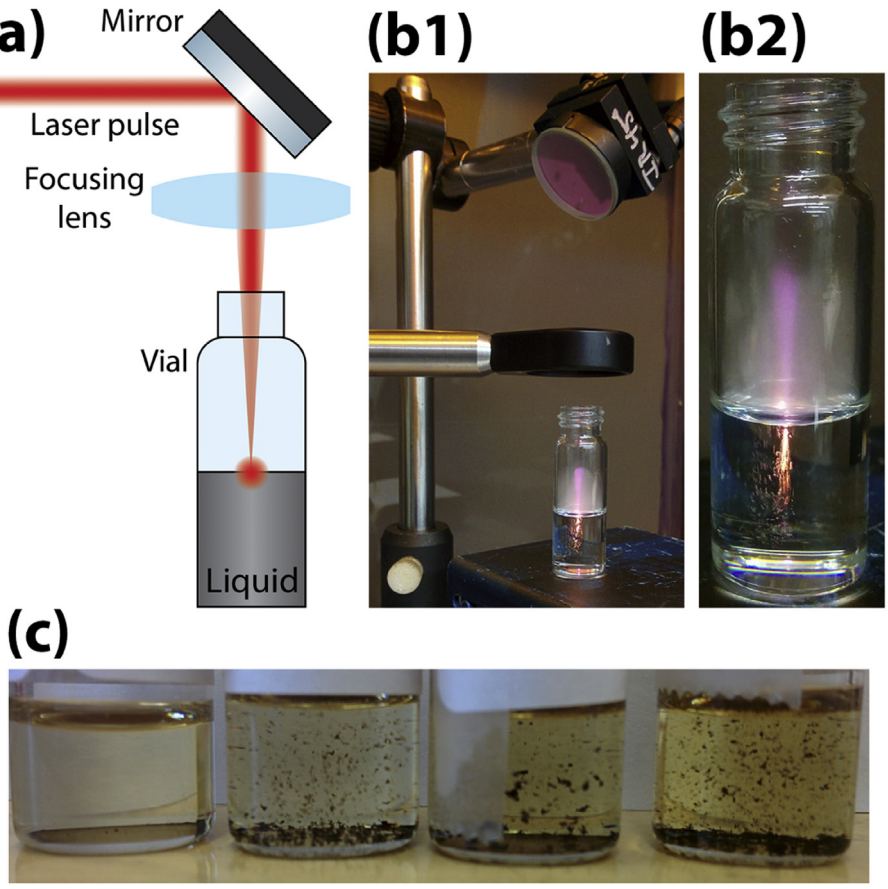

Fig. 1. **(a)** schematic of the toluene irradiation experimental setup. **(b1)** a photograph of the experimental setup with the mirror, lens, and vial visible. The infrared laser pulses are not captured by the camera. **(b2)** a close-up of the toluene in the vial as it is irradiated. As the laser pulse enters the liquid it causes violent turbulence and generates a supercontinuum spectrum. Also, a small amount of liquid is ejected creating a region of toluene vapor that scatters the laser light, making it more visible to the camera. **(c)** samples irradiated for 1, 2, 3, and 4 h respectively, starting from the leftmost vial. The volume of liquid in the vial remains constant throughout the irradiation. (A colour version of this figure can be viewed online.)

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