Tetrahedron Letters 51 (2010) 3221–3225

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Synthesis of end-cap precursor molecules for (6, 6) armchair and (9, 0) zig-zag single-walled carbon nanotubes

Andreas Mueller, Konstantin Yu. Amsharov, Martin Jansen *

Max Planck Institute for Solid State Research, Heisenbergstrasse 1, 70569 Stuttgart, Germany

ARTICLE INFO

Article history:
Received 19 March 2010
Accepted 12 April 2010
Available online 24 April 2010

ABSTRACT

We report the synthesis and purification of a $C_{60}H_{30}$ precursor molecule for the end-cap of a (6, 6) armchair and of a $C_{54}H_{24}$ precursor molecule for a (9, 0) zig-zag type single-walled nanotube. An approach to controlled growth of single-walled carbon nanotubes is suggested.

1. Introduction

Since the advent of carbon nanotubes (CNTs) in 1991,[1] these molecules have attracted a lot of interest in science. They can be thought of as graphene sheets rolled up to seamless cylinders of variable diameters and in principle infinite length. Depending on the number of concentrically arranged tubes, CNTs are denominated as single-walled (SWCNT), double-walled (DWCNT), or multi-walled (MWCNT) carbon nanotubes. SWCNTs are either of semiconducting or metallic type, depending on the orientation of the hexagonal lattice relative to the tube axis, as classified by the chiral indices (n, m).[2] Their unique molecular structures and the resulting extraordinary electronic, thermal, and mechanical properties make them promising candidates for future electronics and composite materials. However, until now all preparation methods result in a mix of different diameters and moreover of different chiralities, thus of both semiconducting and metallic types, which is a serious drawback for the fields of application mentioned. In order to meet such a strong challenge it is logical to start with directing the synthesis of CNTs toward the desired species. Herein lies one of the big challenges of nanotube synthesis. Despite recent advances in the metal-catalyzed synthesis of SWCNTs with specific structural characteristics,[3–9] complete and rational control of the length, diameter, and chirality has still not been achieved. Although there are studies pointing out a dependence of a CNT's diameter on the particle size of the used catalytic particle, and thus a certain diameter control can be achieved, it is still not possible to selectively synthesize isomerically pure CNTs.[9]

According to recent theoretical work by several groups investigating the very first steps of CNT synthesis,[10–12] growth of SWCNTs starts by nucleation of an end-cap fragment on the catalyst particle followed by subsequent growth through incorporation of carbon atoms from the metal surface or bulk. This growth mechanism is known as root-growth. Recently, other groups were able to observe these two steps, the nucleation of a CNT end-cap and subsequent growth in situ in an environmental TEM at temperatures of about 600 °C.[13,14] Considering this growth mechanism of CNTs, it appears to be attractive to avoid the usual nucleation step of CNTs leading to the formation of an end-cap with accidental geometry by introducing a predefined end-cap molecule whose structure can be fully controlled. Subsequent growth will lead to the desired SWCNT species as determined by the end-cap geometry. Steps in this direction were recently reported by Scott's group by the synthesis of a possible precursor molecule for the formation of a (6, 6) armchair nanotube which they aimed to cyclize by flash vacuum pyrolysis (FVP).[15] Although FVP gives reasonable yields of geodesic structures using precursors of low molecular weight, an increase in mass is accompanied by a decreasing yield.[16–20] Thus corannulene ($C_{20}H_{12}$) was obtained with 40% yield and the buckybowl circumtrindene ($C_{36}H_{12}$) was obtained in 27% yield, whereas C_{60} fullerene gave just 0.1–1% yield.[21] Higher fullerenes were only detected by mass spectrometry.[22,23] Besides low yields, appropriate purification which is needed for selective growth of SWCNTs, may pose another problem, especially in case of non or low soluble end-cap molecules.

The discovery of high efficiency catalytic dehydrogenation opens new horizons in that direction. Otero et al. and Rim et al. recently demonstrated methods for the cyclodehydrogenation of polyaromatic hydrocarbons (PAH) to form geodesic polyarenes or even C_{60}.[24,25] The former showed that C_{60} precursor molecules can be condensed to C_{60} by catalytic cyclodehydrogenation on a platinum surface while the latter used a ruthenium surface to condense hexabenzocoronene into a buckybowl. This method for cyclodehydrogenation of PAHs was reported to have a conversion efficiency of 100%.

Taking into consideration that SWCNTs can be grown from thin metal catalyst layers, including Pt-thin films,[26] which are predeposited on a substrate, the scenario as schematized in Figure 1 appears appealing to us. In a first step the right precursor molecule

---

* Corresponding author. Tel.: +49 0 711 689 1501; fax: +49 0 711 689 1502.
E-mail address: m.jansen@fkf.mpg.de (M. Jansen).

0040-4039/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2010.04.055

has to be synthesized, which is subsequently deposited on top of the substrate covered with the appropriate metal catalyst thin-film, then converted to the end-cap, and finally this way predefined SWCNTs can be grown. The use of catalytic dehydrogenation of the precursor molecule directly on the catalytic material instead of applying flash vacuum pyrolysis has, in our opinion, significant advantages over the approach as suggested by Scott's group. The conversion yield to the end-cap is expected to be close to 100%. It should also be pointed out that in order to achieve this high yield there is no need for additional radical promoters on the precursor molecule which are commonly used to increase the conversion efficiency in FVP syntheses. This facilitates the synthesis of the precursor. Further using a flat molecule there is no risk of depositing the end-cap upside-down on the substrate.

In this work we report the synthesis of two end-cap precursor molecules for different types of SWCNTs, that is, $C_{60}H_{30}$ as a possible precursor for a (6, 6) SWCNT, which is of armchair type, and $C_{54}H_{24}$ for a (9, 0) SWCNT, which is of zig-zag type (see Fig. 2). Both precursor molecules would lead to metallic SWCNTs.

2. Results and discussion

The synthetic route of the (6, 6) precursor (**P1**) is presented in Figure 3. 6-Methyl-benzo[*c*]phenanthrene was prepared according to Ref. 27 by standard Wittig olefination of 2-acetonaphthone resulting in the benzostilbene and subsequent Mallory photocyclization using the Katz improvement.[28,29] Benzylic bromination with *N*-bromosuccinimide and subsequent treatment with

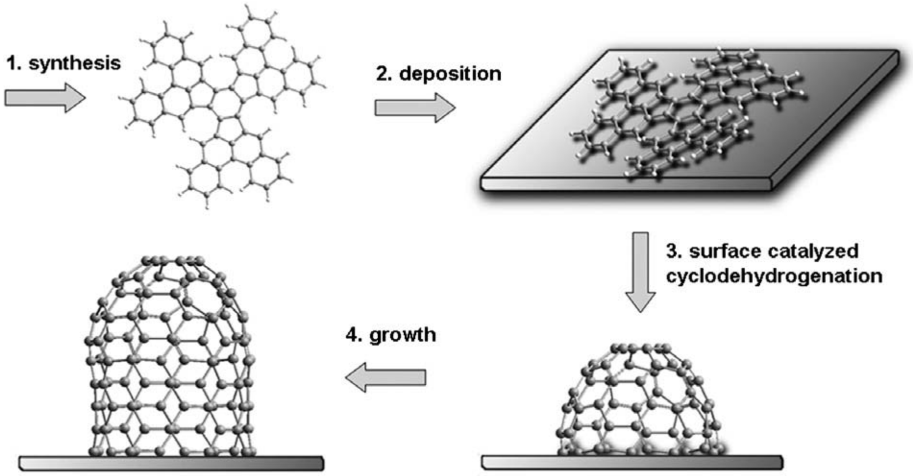

Figure 1. General scheme for the cyclodehydrogenation of the SWCNT end-cap precursor molecules and the subsequent growth of the CNT.

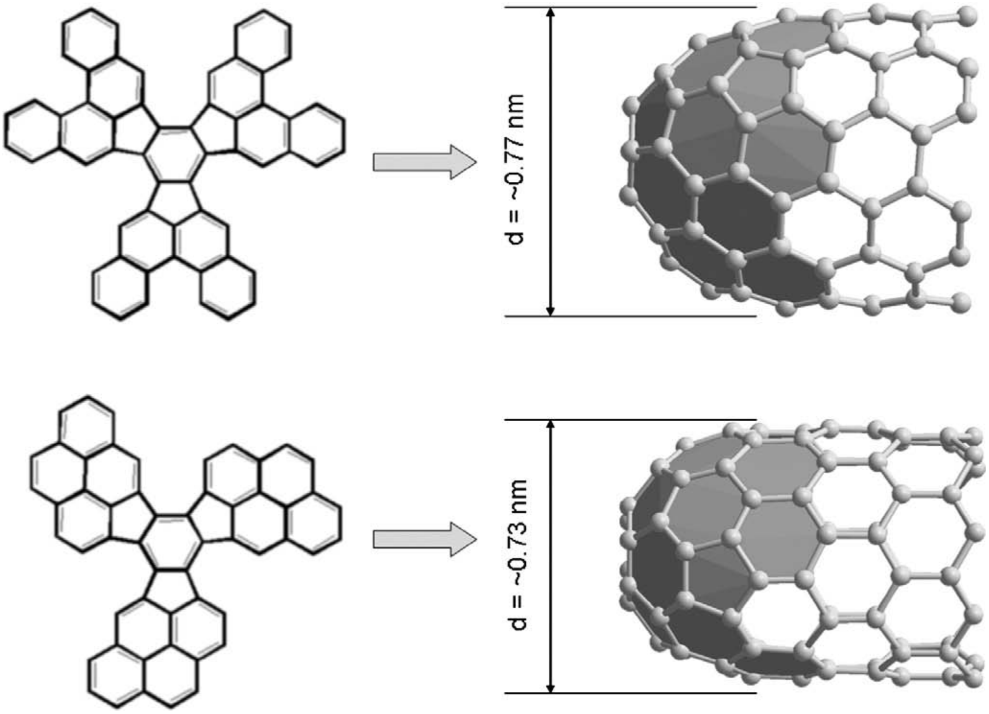

Figure 2. Precursor molecules **P1** for a (6, 6) SWCNT end-cap of armchair type and **P2** for a (9, 0) SWCNT end-cap of zig-zag type; on the right side the corresponding SWCNT structures with the end-caps (gray shaded parts) are shown.

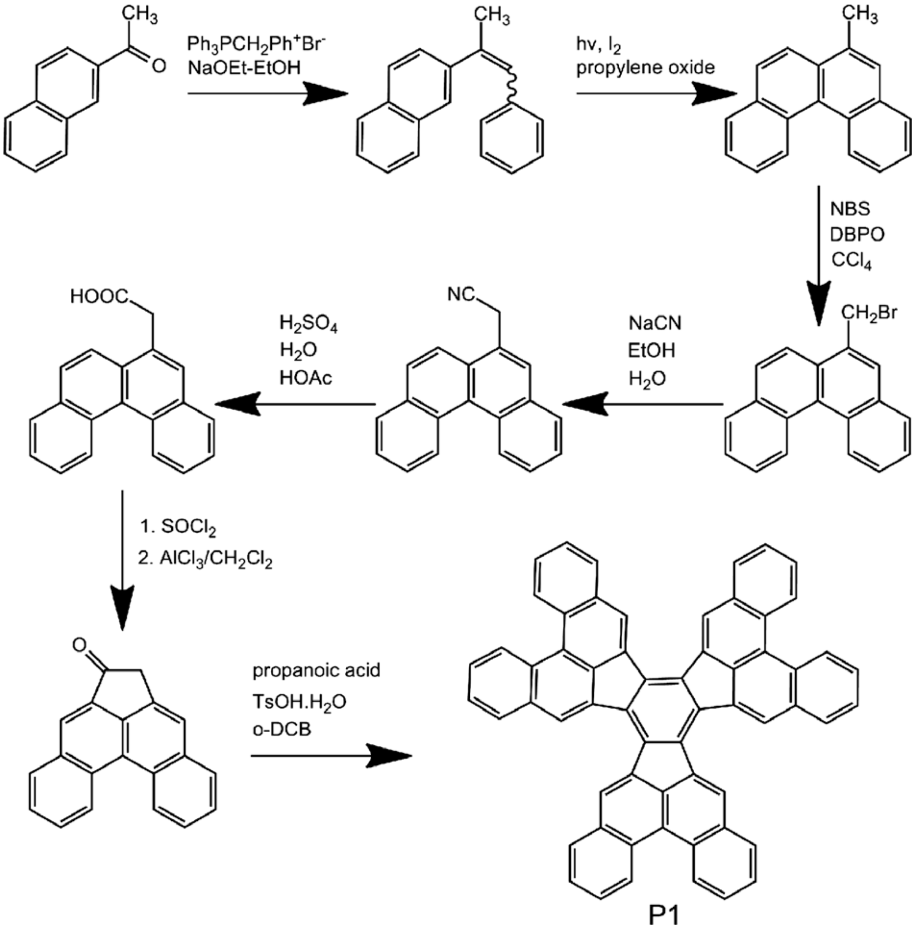

Figure 3. Synthetic route to the $C_{60}H_{30}$ precursor **P1**.

aqueous ethanolic sodium cyanide gave cyanomethylbenzo[*c*]phenanthrene. The product was hydrolyzed into acid and was cyclized in two steps by first transforming benzo[*c*]phenanthrenylacetic acid into the acid chloride and finally performing a Friedel–Crafts acylation leading to ring-closure. For the last synthesis step to turn the monomer into the desired product by aldol trimerization either titanium tetrachloride or Brønsted acid conditions as described by Hill et al. were used.[15] In both cases a reasonable yield of 40% of the precursor P1 was obtained. Under Brønsted acid conditions the trimerization was performed for different solvent/ketone molar ratios and reaction temperatures. At a solvent/ketone molar ratio of 284:1 at 180 °C we obtained the trimer as a yellow powder with high purity and good yield. Single crystals of P1 suitable for X-ray analysis were obtained directly during trimerization at 160 °C with a solvent/ketone molar ratio of about 44:1. This allowed us to confirm the molecular structure of the targeted molecule directly by using X-ray structural analysis (Fig. 4). However, at these latter synthesis conditions the main product was the dimer. This can be understood by looking at the reaction mechanism according to which first the dimer forms which then reacts with a monomer to the trimer.[15,30] In the case of a low molar ratio solvent/ketone the concentration of the dimer produced is exceeding its solubility, starts to precipitate, and thus does not continue to react to the desired trimer.

For the synthesis of the (9, 0) precursor **P2** we used a photochemical route presented in Figure 5 including only three synthetic steps. 1-(Bromoacetyl)pyrene was obtained by a Friedel–Crafts acylation of bromoacetyl bromide and pyrene and subsequently cyclized by UV-radiation through a Pyrex filter according to Spijker et al.[31] As for the synthesis of the (6, 6) precursor, aldol trimerization under Brønsted acid conditions was used to trimerize the ketone into the desired $C_{54}H_{24}$ PAH. The product was purified by

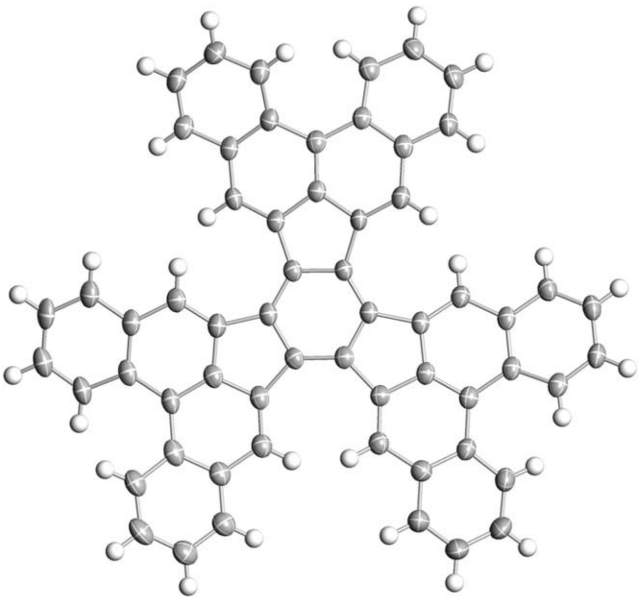

Figure 4. Molecular structure of the $C_{60}H_{30}$ precursor **P1** as determined from single-crystal X-ray diffraction data.

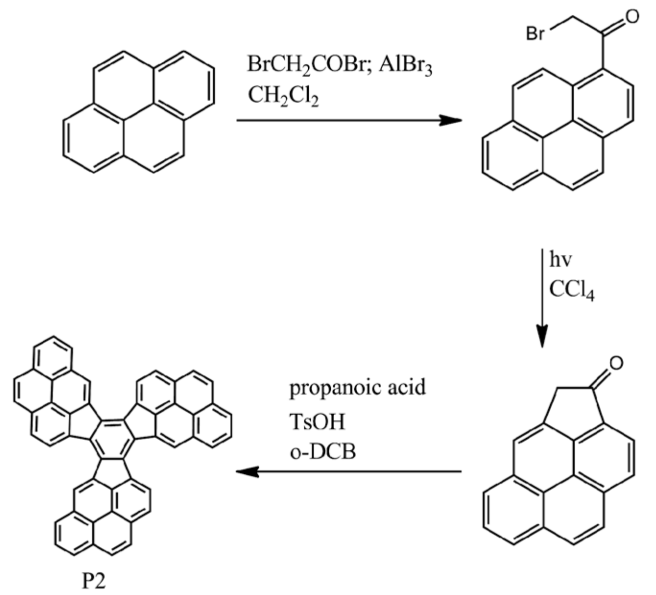

Figure 5. Synthetic route to the $C_{54}H_{24}$ precursor **P2**.

sublimation. The LDI-TOF mass spectrometry analysis gave almost exclusively a signal at 672.26 *m*/*z* which strongly indicates the formation of the desired trimer (Fig. 6).

For the purpose that the two molecules are intended, their purity is a very crucial issue. Both precursors were found to be non soluble in common solvents and poorly soluble in 1,2,4-trichlorobenzene or hot *o*-dichlorobenzene which prevented purification by chromatographic methods or recrystallization. Nevertheless it was found that high temperature sublimation (400 °C) using rather low vacuum (10^{-2} mbar) of both compounds gave the desired products in high purity as was confirmed by LDI-TOF analysis (see Supplementary data Figs. S2 and S4). This is indicative of a high thermostability of the desired products compared to the byproducts like dimer, tetramer, or polymers.

In summary we have synthesized end-cap precursor molecules for two types of metallic single-wall carbon nanotubes, one for a (6, 6) nanotube of armchair type and a second for a (9, 0) nanotube of zig-zag type. Further we show that these molecules can be obtained with high purity by applying high temperature sublimation. The synthesized precursor molecules will be used for the proposed SWCNT synthesis scenario.

3. Experimental section

Mass spectra were recorded with a Shimadzu AXIMA resonance spectrometer in positive mode. The single crystal data were collected with a dual wavelength diffractometer system using an Incoatec microfocus X-ray source IμS (Cu Kα radiation, $\lambda = 1.54178$ Å). More details of the diffractometer setup can be found elsewhere.[32] The structure was solved by direct methods and refined by fullmatrix least-squares fitting with the SHELXTL software package.[33] IR spectra were measured with a Bruker IFS 113 V FT-IR spectrometer.

Experimental procedures for the synthetic pathways up to oxo-6,7-acebenzo[*c*]phenanthrene and cyclopenta[*cd*]pyren-3(4*H*)-one can be found in Supplementary data.

3.1. Trimerization of oxo-6,7-acebenzo[*c*]phenanthrene (P1)

A mixture of oxo-6,7-acebenzo[*c*]phenanthrene (20 mg, 0.075 mmol), *p*-toluene sulfonic acid monohydrate (54 mg, 0.284 mmol), propionic acid (0.02 ml), and *o*-dichlorobenzene (2.4 ml) was transferred in a glass ampoule of 1 cm in diameter. The glass ampoule was evacuated and sealed by melting while the reaction mixture was frozen by liquid nitrogen to prevent the solvent from evaporation. The mixture was heated at 180 °C for 16 h. After cooling down the glass ampoule a black liquid was yielded and a yellow precipitate could be observed. The mixture was poured into 50 ml of methanol. Addition of aqueous NaOH solution resulted in a precipitate which was subsequently vacuum filtrated and washed with methanol, H_2O, acetone, CH_2Cl_2, and

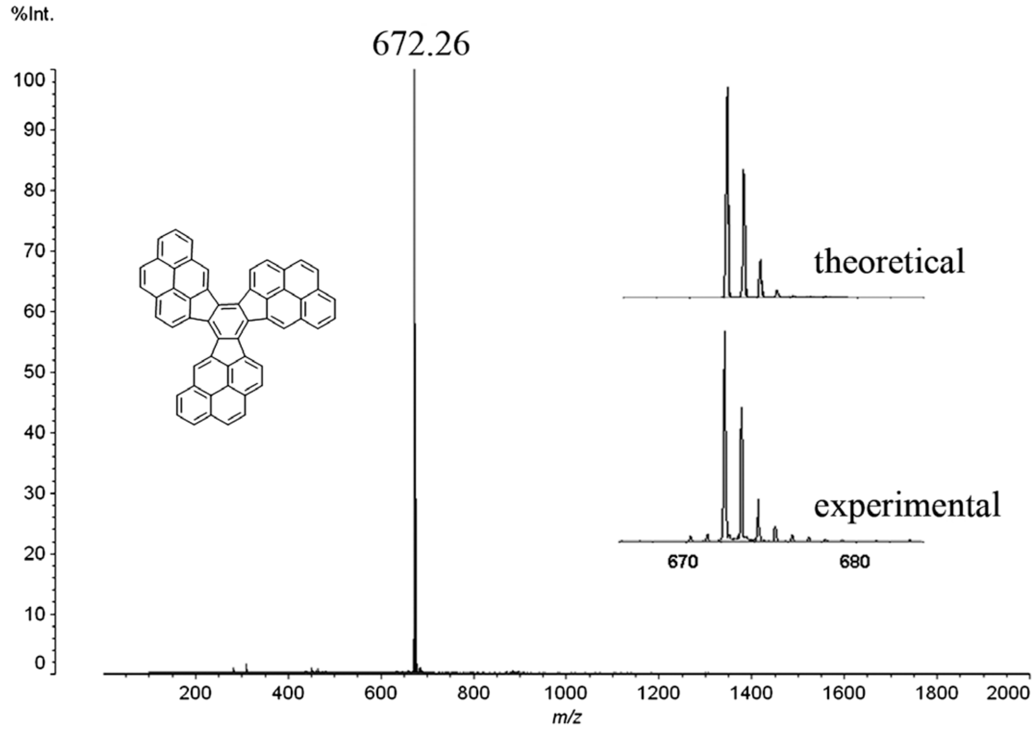

Figure 6. LDI-TOF analysis of purified precursor **P2** after trimerization of cyclopenta[*cd*]pyren-3(4*H*)-one, positive mode.

petroleumether resulting in a yellow powder (8 mg, 40% yield). Further purification was done by sublimation at 400 °C and 10^{-2} mbar giving a yellow sublimate. LDI-TOF MS: $m/z = 750.31$ $[M]^+$ (Exact Mass: 750.2348). UV–vis: $\lambda_{\max}$ (1,2,4-trichlorobenzene)/[nm] = 330, 382, 406, 431. Crystal data: monoclinic space group $C2/c$, $a = 33.444(3)$, $b = 9.5755(9)$, $c = 27.512(2)$ Å, $\beta = 119.131(4)°$, $V = 7696.1(12)$ Å^3, $Z = 8$ $2\theta_{\max} = 130.01°$, $-39 < h < 37$, $-9 < k < 10$, $-31 < l < 32$, $\lambda = 1.54178$ Å, $T = 100(2)$ K, final $R_1 = 0.0608$ ($R_2(w) = 0.1809$). CCDC-761361 contains the supplementary crystallographic data for this Letter. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3.2. Trimerization of cyclopenta[*cd*]pyren-3(4*H*)-one (P2)

Cyclopenta[*cd*]pyren-3(4*H*)-one (0.02 g, 0.083 mmol) was transferred together with *p*-toluenesulfonic acid monohydrate (0.05 g, 0.26 mmol) and propanoic acid (0.02 ml) into a sealable glass tube. After the addition of *o*-dichlorobenzene (2.4 ml), the tube was evacuated, sealed, and heated to 180 °C for 16 h. The resulting black liquid was put into methanol, and aqueous NaOH solution was added. The resulting precipitate was filtered and washed with methanol, H_2O, acetone, CH_2Cl_2, and petroleumether resulting in a brown powder (12.3 mg, 61% yield). Purification was done by sublimation at 400 °C and 10^{-2} mbar resulting in an orange sublimate. LDI-TOF MS: $m/z = 672.26$ $[M]^+$ (Exact Mass: 672.1878). UV–vis: $\lambda_{\max}$ (1,2,4-trichlorobenzene)/[nm] = 358, 379, 400, 469.

Acknowledgment

We thank Dr. J. Nuss for collecting the X-ray data.

Supplementary data

Supplementary data (experimental procedures for synthetic pathways up to oxo-6,7-acebenzo[*c*]phenanthrene and cyclopenta[*cd*]pyren-3(4*H*)-one are provided with according ^{1}H NMR and ^{13}C NMR data. The crystal packing structure for $C_{60}H_{30}$ is shown. For both precursors **P1** and **P2** LDI-TOF mass spectra are shown before and after purification by high temperature sublimation. UV–vis and IR spectra are provided for both precursors) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.04.055.

References and notes

1. Iijima, S. *Nature* **1991**, *354*, 56–58.
2. Meyyappan, M. *Carbon Nanotubes: Science and Application*; CRC Press LLC: Boca Raton, London, New York, Washington, DC, 2005. Chapter 1.
3. Maruyama, S.; Kojima, R.; Miyauchi, Y.; Chiashi, S.; Kohno, M. *Chem. Phys. Lett.* **2002**, *360*, 229–234.
4. Bachilo, S. M.; Balzano, L.; Herrera, J. E.; Pompeo, F.; Resasco, D. E.; Weisman, R. B. *J. Am. Chem. Soc.* **2003**, *125*, 11186–11187.
5. Lu, C. G.; Liu, J. *J. Phys. Chem. B* **2006**, *110*, 20254–20257.
6. Hata, K.; Futaba, D. N.; Mizuno, K.; Namai, T.; Yumura, M.; Iijima, S. *Science* **2004**, *306*, 1362–1364.
7. Huang, S. M.; Woodson, M.; Smalley, R.; Liu, J. *Nano Lett.* **2004**, *4*, 1025–1028.
8. Yamada, T.; Namai, T.; Hata, K.; Futaba, D. N.; Mizuno, K.; Fan, J.; Yudasaka, M.; Yumura, M.; Iijima, S. *Nat. Nanotechnol.* **2006**, *1*, 131–136.
9. Choi, H. C.; Kim, W.; Wang, D. W.; Dai, H. J. *J. Phys. Chem. B* **2002**, *106*, 12361–12365.
10. Ohta, Y.; Okamoto, Y.; Irle, S.; Morokuma, K. *J. Phys. Chem. C* **2009**, *113*, 159–169.
11. Gavillet, J.; Loiseau, A.; Journet, C.; Willaime, F.; Ducastelle, F.; Charlier, J. C. *Phys. Rev. Lett.* **2001**, *87*, 275504-1–275504-4.
12. Raty, J. Y.; Gygi, F.; Galli, G. *Phys. Rev. Lett.* **2005**, *95*, 096103-1–096103-4.
13. Hofmann, S.; Sharma, R.; Ducati, C.; Du, G.; Mattevi, C.; Cepek, C.; Cantoro, M.; Pisana, S.; Parvez, A.; Cervantes Sodi, F.; Ferrari, A. C.; Dunin-Borkowski, R.; Lizzit, S.; Petaccia, L.; Goldoni, A.; Robertson, J. *Nano Lett.* **2007**, *7*, 602–608.
14. Yoshida, H.; Takeda, S.; Uchiyama, T.; Kohno, H.; Homma, Y. *Nano Lett.* **2008**, *8*, 2082–2086.
15. Hill, T. J.; Hughes, R. K.; Scott, L. T. *Tetrahedron* **2008**, *64*, 11360–11369.
16. Tsefrikas, V. M.; Scott, L. T. *Chem. Rev.* **2006**, *106*, 4868–4884.
17. Mehta, G.; Rao, H. S. P. *Tetrahedron* **1998**, *54*, 13325–13370.
18. Plater, M. J.; Praveen, M.; Schmidt, D. M. *Fullerene Sci. Technol.* **1997**, *5*, 781–800.
19. Scott, L. T. *Pure Appl. Chem.* **1996**, *68*, 291–300.
20. Scott, L. T. *Angew. Chem., Int. Ed.* **2004**, *43*, 4994–5007.
21. Scott, L. T.; Boorum, M. M.; McMahon, B. J.; Hagen, S.; Mack, J.; Blank, J.; Wegner, H.; de Meijere, A. *Science* **2002**, *295*, 1500–1503.
22. Amsharov, K.; Jansen, M. *Chem. Commun.* **2009**, 2691–2693.
23. Amsharov, K. Y.; Jansen, M. *J. Org. Chem.* **2008**, *73*, 2931–2934.
24. Otero, G.; Biddau, G.; Sanchez-Sanchez, C.; Caillard, R.; Lopez, M. F.; Rogero, C.; Palomares, F. J.; Cabello, N.; Basanta, M. A.; Ortega, J.; Mendez, J.; Echavarren, A. M.; Perez, R.; Gomez-Lor, B.; Martin-Gago, J. A. *Nature* **2008**, *454*, 865–868.
25. Rim, K. T.; Siaj, M.; Xiao, S. X.; Myers, M.; Carpentier, V. D.; Liu, L.; Su, C. C.; Steigerwald, M. L.; Hybertsen, M. S.; McBreen, P. H.; Flynn, G. W.; Nuckolls, C. *Angew. Chem., Int. Ed.* **2007**, *46*, 7891–7895.
26. Takagi, D.; Homma, Y.; Hibino, H.; Suzuki, S.; Kobayashi, Y. *Nano Lett.* **2006**, *6*, 2642–2645.
27. Magnus, P.; Morris, J. C.; Lynch, V. *Synthesis* **1997**, 506–508.
28. Nagel, D. L.; Kupper, R.; Antonson, K.; Wallcave, L. *J. Org. Chem.* **1977**, *42*, 3626–3628.
29. Liu, L. B.; Yang, B. W.; Katz, T. J.; Poindexter, M. K. *J. Org. Chem.* **1991**, *56*, 3769–3775.
30. Amick, A. W.; Scott, L. T. *J. Org. Chem.* **2007**, *72*, 3412–3418.
31. Spijker, N. M.; Vandenbrakenvanleersum, A. M.; Lugtenburg, J.; Cornelisse, J. A. *J. Org. Chem.* **1990**, *55*, 756–758.
32. Cakmak, G.; Nuss, J.; Jansen, M. *Z. Anorg. Allg. Chem.* **2009**, *635*, 631–636.
33. Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122. Lyle, F. R., U.S. Patent 5 973 257, 1985; *Chem. Abstr.* **1985**, *65*, 2870.