DOI: 10.1002/ejoc.200700630

Novel Approach to Stabilize Unstable Molecular Wires by Simultaneous Rotaxane Formation – Synthesis of Inclusion Complexes of Oligocarbynes with Cyclic Host Molecules

Jiro Sugiyama[a] **and Ikuyoshi Tomita***[a]

Keywords: Rotaxane / Cyclodextrin / Inclusion compounds / Carbynes

An effective method to stabilize oligocarbynes as a model for polycarbyne by the simultaneous complexation with α-cyclodextrin (α-CD) is described. 1,12-Bis(9-phenanthryl)-1,3,5,7,9,11-dodecahexayne possessing one or two α-CD molecules was prepared by the oxidative coupling reaction of the corresponding triyne in the presence of α-CD. The resulting rotaxanes proved to be stable enough in comparison with the corresponding free oligoynes.

Introduction

Among polymers possessing π-conjugated repeating units, polycarbyne has the simplest one-dimentional structure, in whitch sp-hybridized carbon atoms are linked through σ- and π-bonds. Despite its potential applications to unique functional materials exhibiting optical, electrical, and mechanical properties, its instability and poor solubility made it difficult to perform the related studies.

One possible approach to improve its stability and poor solubility is to introduce appropriate end groups on both ends of the carbyne chains. Whiting et al. have described the synthesis and characterization of a series of oligoynes having phenyl end groups with up to eight triple bonds. UV/Vis spectra of the series of oligoynes suggested the effective π-conjugation along the acetylene units, because the wavelength of each absorption band shows a clear bathochromic shift by the elongation of the acetylene units.[1a] An almost linear alignment of the carbyne chain has been supported by the single-crystal X-ray structural investigation of oligoynes such as 1,10-diphenyl-1,3,5,7,9-decapentayne[1b] and 1,12-diphenyl-1,3,5,7,9,11-dodecahexayne.[1c] Hirsh and co-workers prepared oligoynes having dendritic end groups, whose stability increased as a function of the bulkiness of the end groups. For example, the third-generation dendrimer-capped molecule having ten acetylene units is stable enough to be isolated and characterized.[1d] Not only the sterically demanding groups, but also organometallic fragments often serve as good end groups for the synthesis of molecules having longer carbyne chains. For example, Gladysz and co-workers reported the synthesis of oligoynes having (pentafluorophenyl)bis(phosphane)platinum end groups, in which oligoynes having up to 16 acetylene units could be successfully isolated and fully characterized.[1e]

However, the stabilization effect of end groups becomes not sufficient if the chain length is increased. In order to obtain much longer carbyne chains as stable molecules, a spatial protection might be required to insulate the carbyne chains form other moecules. Gladysz et al. reported a novel method to insulate the carbyne chains possessing platinum moieties on both ends by use of bis(phosphanyl)alkanes in which alkane chains are supposed to insulate each carbyne chain by the formation of a double-helix conformation around the carbyne chain.[1f] Nevertheless, this method may also require sequential synthetic steps, which would limit the length of the carbyne chain by the instability of "naked" intermediates.

As an alternative method, we are trying to stabilize and to solubilize the carbyne chains by simultaneous formation of pseudo-rotaxanes and rotaxanes with cyclodextrin (CD).[2] Herein, we wish to show this possibility using oligoynes as preliminary models of polycarbyne.

Results and Discussion

As oligoynes for the present study, we employed 1,3,5,7,9,11-dodecahexaynes (C12) having two aromatic substituents on α- and ω-positions [i.e., 1,12-diphenyl- (P-C12) and 1,12-bis(9-phenanthryl)- (PH-C12), Figure 1], because their moderate instability both in bulk and solution at ambient conditions is suitable to demonstrate the stabilization effect.

---

[a] Tokyo Institute of Technology, Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering
4259-G1-9 Nagatsuta-cho, Midori-ku, Yokohama, 226-8502, Japan
Fax: +81-45-924-5489
E-mail: tomita@echem.titech.ac.jp

Supporting information for this article is available on the WWW under http://www.eurjoc.org or from the author.

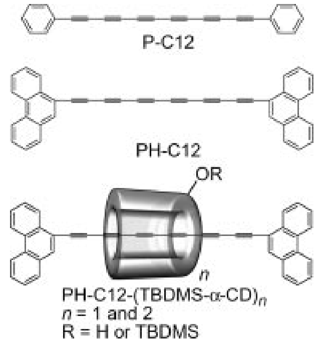

Figure 1. Structure of oligoynes [P-C12, PH-C12, and PH-C12-(TBDMS-α-CD)$_n$].

The UV/Vis absorption spectra of P-C12 taken in a dilute solution of *N*,*N*-dimethylformamide (DMF) ($[\text{P-C12}]_0 = 1.0 \times 10^{-5}$ м) exhibits a gradual irreversible change after 1 h, indicating that intermolecular reactions occur under the examined conditions (Figure 2a).[5] On the other hand, the corresponding change could be suppressed significantly in the presence of an excess amount of α-CD ($[\alpha\text{-CD}]_0 = 1.0 \times 10^{-3}$ м) (Figure 2b). The result can be taken to mean that the formation of a pseudo-rotaxane of P-C12 and α-CD takes place simply by mixing the two compounds in DMF, which is effective to stabilize P-C12 by preventing it from intermolecular crosslinking reactions. In this case, however, an excess amount of α-CD is required to stabilize P-C12 (e.g., stoichiometric conditions; Figure 2c), because the complex of P-C12 and α-CD, a pseudo-rotaxane, is in an equilibrium with the dissociated form.

The complexation also takes place by bringing in contact the crystals of P-C12 with an aqueous solution of α-CD (0.15 м) under ultrasonication conditions. From the UV/Vis spectra of the water-soluble part obtained by filtration of the emulsified product, the characteristic absorption bands of P-C12 were observed.[6] Hexagonal crystals of the pseudo-rotaxane of P-C12 and α-CD were obtained by recrystallization of an aqueous solution. The crystals exhibited higher thermal stability than the "naked" P-C12 judging from the measurements with an optical microscope equipped with a hot stage. That is, the crystals did not show a color darkening below 270 °C (i.e., the melting point of α-CD), while the free P-C12 exhibited a noticeable color change above 130 °C and the resulting dark sample was insoluble in organic solvents.

In order to stabilize oligocarbynes more effectively, the simultaneous synthesis of rotaxane molecules was performed by locking α-CD with much sterically demanding end groups. That is, a hexayne having phenanthryl substituents on both ends (PH-C12) was prepared by oxidative coupling reaction of a 1:1 pseudo-rotaxane of 1-phenanthryl-1,3,5-hexatriyne (PH-C6-H)/α-CD in a mixed solvent of DMF/H_2O (1:2, v/v) containing α-CD (3 equiv.).[7] The rotaxanes are insoluble in water and many organic solvents except that they could be dissolved slightly in DMF. Thus, the chemical modification of the hydroxy groups of the α-CD units was performed using *tert*-butyldimethylsilyl chloride/imidazole to improve their solubility. Consequently, rotaxanes of PH-C12 possessing one and two α-CD molecules [PH-C12-(TBDMS-α-CD)$_1$ and PH-C12-(TBDMS-α-CD)$_2$] were produced in 12% and 17% yields, respectively. Under the examined reaction conditions, about 61% and 51% of the hydroxy groups of these rotaxanes could be silylated, and the resulting rotaxanes [PH-C12-(TBDMS-α-CD)$_1$ and PH-C12-(TBDMS-α-CD)$_2$, respectively] exhibited good solubility in common organic solvents such as chloroform and THF.

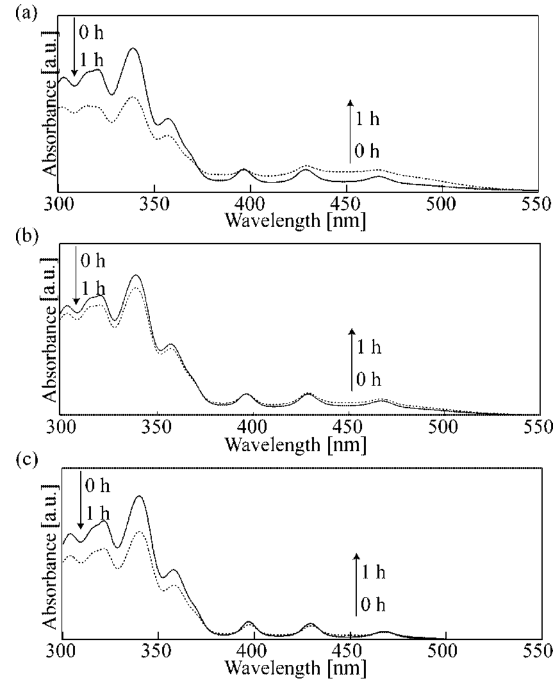

Figure 2. Change in the UV/Vis absorption spectra of P-C12 in DMF without (a) and with (b, c) α-CD after 1 h at ambient temperature {conditions: $[\text{P-C12}]_0 = 1.0 \times 10^{-5}$ м, $[\alpha\text{-CD}]_0 = 0$ м (a), 1.0×10^{-3} м (b), and 1.0×10^{-5} м (c)}.

A remarkable stabilization effect of α-CD is clearly observable from the time-course UV/Vis absorption spectra of PH-C12-(TBDMS-α-CD)$_1$ and PH-C12-(TBDMS-α-CD)$_2$ in DMF: the spectra of both PH-C12-(TBDMS-α-CD)$_1$ and PH-C12-(TBDMS-α-CD)$_2$ exhibit no significant change on keeping at ambient temperature for 1 h (Figure 3b and Figure 3c), while the "naked" PH-C12 is somewhat unstable under the same conditions (Figure 3a). It is also of note that the bulky phenanthryl groups prohibit the unthreading of α-CD, leading to a much more effective stabilization of the oligocarbyne in comparison with the case of the pseudo-rotaxane of P-C12.

In summary, we reported a method to stabilize oligoynes not by direct structural modification but by "simultaneous formation of an inclusion complex with α-CD". Since the complexation with α-CD is confirmed to be a quite effective method to improve the stability of oligocarbynes, we are currently trying to extend the chain length of the carbyne system and elucidate the nature of this series of unique functional materials.

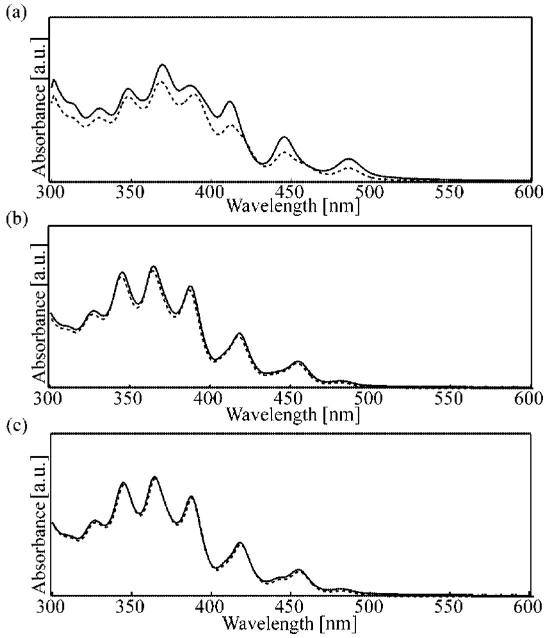

Figure 3. UV/Vis absorption spectra of PH-C12 (a), PH-C12-(TBDMS-α-CD)$_1$ (b), and PH-C12-(TBDMS-α-CD)$_2$ (c) in DMF before (solid line) and after 1 h (dotted line) {conditions: [PH-C12]$_0$ = [PH-C12-(TBDMS-α-CD)$_1$]$_0$ = [PH-C12-(TBDMS-α-CD)$_2$]$_0$ = 1.0×10^{-5} M, at ambient temperature}.

Supporting Information (see footnote on the first page of this article): Experimental details, ^{1}H NMR spectra of TBDMS-α-CD, photographs of crystals of the pseudorotaxanes.

---

[1] a) J. B. Armitage, N. Entwisle, E. R. H. Jones, M. C. Whiting, *J. Chem. Soc.* **1954**, 147; b) Y. Rubin, S. S. Lin, C. B. Knobler, J. Anthony, A. M. Boldi, F. Diederich, *J. Am. Chem. Soc.* **1991**, *113*, 6943–6949; c) T. Luu, E. Elliott, A. D. Slepkov, S. Eisler, R. McDonald, F. A. Hegmann, R. R. Tykwinski, *Org. Lett.* **2004**, *7*, 51–54; d) A. Gibtner, F. Hampel, J. Gisselbrecht, A. Hirsh, *Chem. Eur. J.* **2002**, *8*, 408–432; e) W. Mohr, J. Stahl, F. Hampel, J. A. Gladysz, *Chem. Eur. J.* **2003**, *9*, 3324–3340; f) J. Stahl, J. C. Bohling, E. B. Bauer, T. B. Peters, W. Mohr, J. M. Alvarez, F. Hampel, J. A. Gladysz, *Angew. Chem. Int. Ed. Engl.* **2002**, *41*, 1871–1876.

[2] There are preceding works on stabilization[3] and improvement of solubility[4] of guest molecules by formation of inclusion complexes with cyclic host molecules.

[3] Some unstable molecules have been reported to be stabilized by the formation of inclusion complexes with cyclic host molecules, see a) J. Buston, J. Young, H. Anderson, *Chem. Commun.* **2000**, 905–906; b) T. Oku, Y. Furusho, T. Takata, *Org. Lett.* **2003**, *5*, 4923–4925.

[4] Improvement of the solubility by the formation of inclusion complexes has also been reported, see: a) H. Dodziuk, A. Ejchart, W. Anczewski, H. Ueda, E. Krinichnaya, G. Dolgonos, W. Kutner, *Chem. Commun.* **2003**, 986–987; b) A. Harada, H. Okumura, M. Okada, S. Suzuki, M. Kamachi, *Chem. Lett.* **2000**, 548–549.

[5] From the MS measurement of a sample kept in DMF for 1 h, degraded products attributable to dimers were observed. Therefore, the change observed in the UV/Vis spectra of P-C12 is at least partly due to oligomerization reactions.

[6] The crystals of P-C12 (0.030 g, 0.10 mmol) were brought in contact with an aqueous solution of α-CD (0.15 M, 5.0 mL) under ultrasonication for 6 h. On the basis of the molar extinction coefficient of the UV/Vis spectrum of P-C12 in DMF ([P-C12]$_0$ = 1.0×10^{-5} M, $\varepsilon = 1.1 \times 10^5$), the concentration of P-C12 in the aqueous solution obtained by filtration of this mixture was estimated to be 1.5×10^{-6} M.

[7] If the oxidative homo-coupling reaction of the free PH-C6-H was performed in the presence of α-CD (i.e., without prior formation of pseudo-rotaxane), the rotaxanes were obtained in lower yields [PH-C12-(TBDMS-α-CD)$_1$: 7%; PH-C12-(TBDMS-α-CD)$_2$: 5%]. Also, if the homo-coupling reaction of the pseudo-rotaxane of PH-C6-H and α-CD was carried out in the absence of an excess amount of α-CD, the rotaxanes were produced in lower yields [PH-C12-(TBDMS-α-CD)$_1$: 5%; PH-C12-(TBDMS-α-CD)$_2$: 4%].

Received: July 9, 2007