JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

pubs.acs.org/JACS

Bottom-up Synthesis and Thread-in-Bead Structures of Finite $(n,0)$-Zigzag Single-Wall Carbon Nanotubes

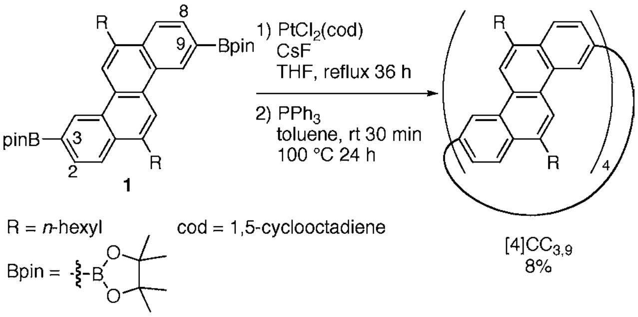
Shunpei Hitosugi, Takashi Yamasaki, and Hiroyuki Isobe*

Department of Chemistry, Tohoku University, Sendai 980-8578, Japan

Ⓢ *Supporting Information*

ABSTRACT: The last remaining synthetic target of finite single-wall carbon nanotube models, the zigzag nanotube, has been accomplished through bottom-up chemical synthesis. The zigzag nanotube was synthetically accessible without constructing long-sought yet elusive cyclacene structures but with a cycloarylene structure by devising its cutout positions. The persistent tubular shape was also perfected in this last model by cyclization of zigzag-shaped aromatic molecules with a synchronous topological arrangement. The crystal structure of this nanotube further revealed an entangled supramolecular assembly, which showed a novel way to align nanotube molecules by utilizing their open-end functional groups in a thread-in-bead molecular assembly.

Scheme 1. Synthesis of $[4]CC_{3,9}$



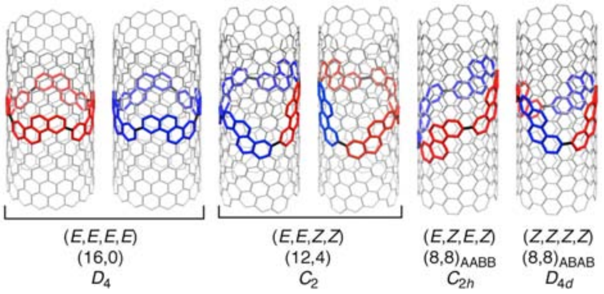


Figure 1. Possible structures of $[4]CC_{3,9}$ embedded in the corresponding SWNT. Two possible chrysenylene orientations are shown in red and blue. Stereoconfigurations at the single-bond linkage, chiral indexes, and point symmetry are shown under the molecular models.

The structures of single-wall carbon nanotubes (SWNT) are classified in three forms, i.e., armchair, helical, and zigzag, which are, respectively, named after the structures of their cross-sectional rings and are defined by their chiral indexes of (n,n), (n,m), and $(n,0)$.[1] The arrangement of sp^2-carbon in a tubular form is so intriguing that it has stimulated intense investigations into the chemical synthesis of finite models with discrete structures to explore the fundamental structural chemistry. After the synthesis of the (5,5)-armchair SWNT model through top-down synthesis from [60]fullerene,[2] a variety of armchair models were generated by the introduction of bottom-up strategies for the synthesis of cycloparaphenylene (CPP) and its congeneric nanohoops to accumulate armchair variants with chiral indexes from $n = 6$ to 18.[3−6] Although the model structure in CPP was not perfected in that the arylene units were rotatable,[7] we recently introduced belt-persistent nanohoops by incorporating chrysenylene in the cycloarylene nanohoops and reported the bottom-up synthesis of (n,m)-helical and (n,n)-armchair SWNT models.[8,9] However, despite these intense studies, the model compound for $(n,0)$-zigzag SWNT has been left blank and thus far remains as the last challenging target for the synthesis. Moreover, theoretical investigations of an apparent, yet elusive, finite model of zigzag SWNT, i.e., cyclacene, also indicated the difficulty in its synthesis by predicting a highly reactive open-shell nature of the cyclacene models.[10,11] Here we report the first synthesis of an $(n,0)$-zigzag SWNT model through the application of the chrysenylene-nanohoop strategy. Devising the cutout positions of zigzag SWNT with chrysenylene panels resulted in the synthesis of the isolable zigzag model with an extreme belt persistency and afforded a single diastereomeric (16,0)-model among four possible diastereomers. We further succeeded in the crystallographic analysis of the finite SWNT and revealed an entangled array of the molecules. The crystal structure showed that the void space of the nanotubes can help in guiding the molecular assembly in a unique thread-in-bead fashion, which may be readily applied to longer SWNT with the open-end modifications.[12]

Departing from the cross-sectional ring of armchair SWNT, the armchair shape gradually inclines through the helical nanotubes and, at the orthogonal end, there appears the zigzag structure (Figure S1).[1] Although this zigzag cross-sectional structure points to cyclacene as an apparent finite zigzag model,[3,10,11] the infinite carbon network of SWNT allowed us to utilize chrysene as the segment. Thus, we started the synthesis of the zigzag model with 3,9-diborylchrysene **1**,[13] but,

Received: June 12, 2012
Published: July 16, 2012

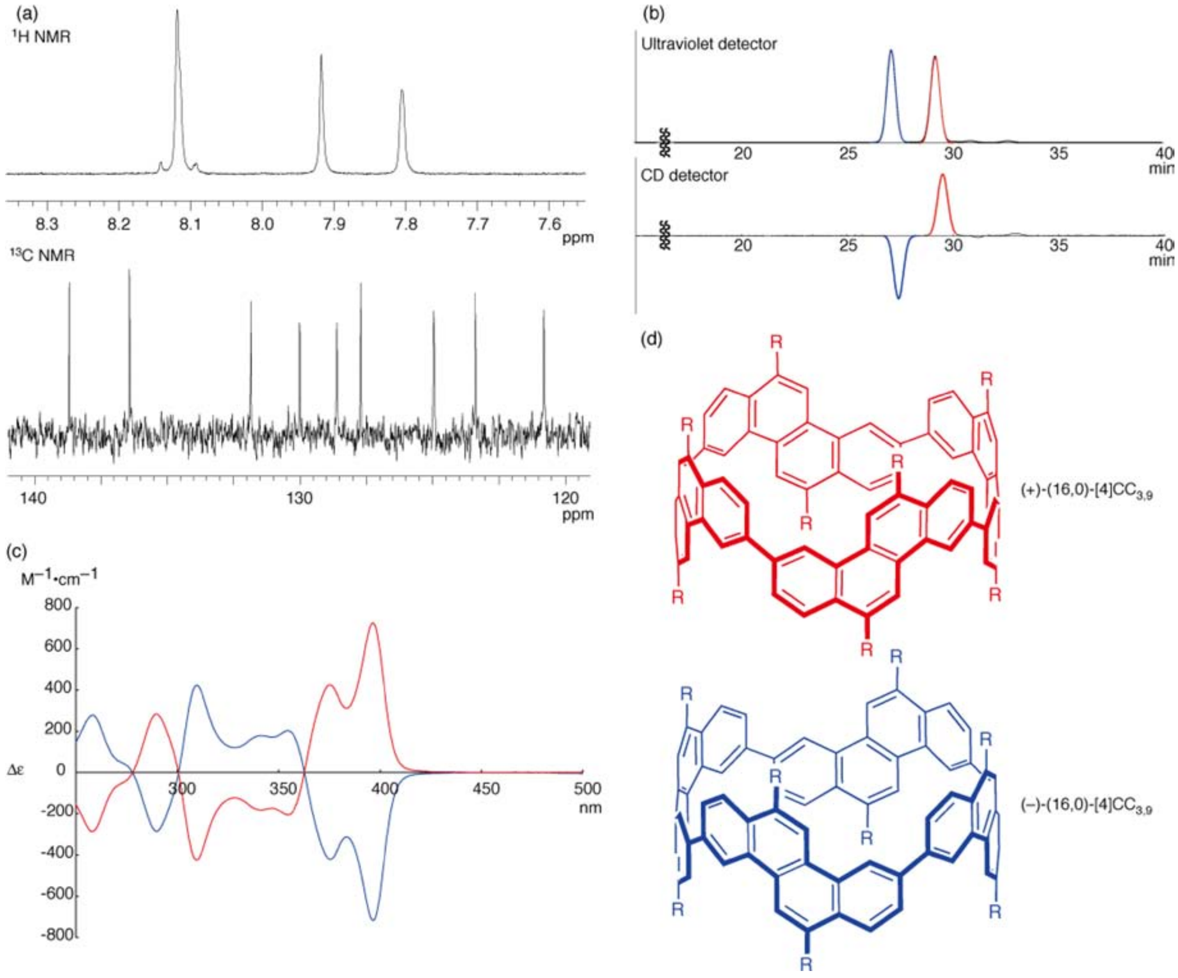


Figure 2. Analysis and structures of $[4]CC_{3,9}$. (a) ^1H and ^{13}C NMR spectra in the aromatic region. See Figure S2 for the whole region. Four and nine signals were detected in ^1H and ^{13}C NMR, respectively. Note that two doublet signals near 8.1 ppm in ^1H NMR are close to each other and therefore highly skewed. (b) HPLC analysis with cholesterylated silica gel columns. The top chart shows the analysis with ultraviolet detection at 300 nm, and the bottom chart shows the simultaneous analysis with CD detection at 420 nm. The (+)-enantiomer displaying a steroid-like surface outward was retained in the column longer (see Figure 2d for the structure).[8] (c) CD spectra of (+)-isomer (red) and (−)-isomers (blue) in chloroform. (d) Structures of $[4]CC_{3,9}$. The absolute configurations were assigned by comparison with theoretical spectra (Figure S6). Note that we used (+)- and (−)-descriptors for the enantiomers due to the lack of appropriate nomenclature for this stereoisomerism. The colors of enantiomers correspond to the molecular model in Figure 1, the HPLC peaks in Figure 2b, and the CD spectra in Figure 2c.

albeit subtle at a glance, the change in the linking points of [4]cyclochrysenylene ([4]CC) unexpectedly affected the synthesis to a considerable extent. Although the previous reaction of $PtCl_2$(cod) with 2,8-diborylchrysene afforded a square-shaped tetrameric complex in good yield,[5,8] the same reaction with the 3,9-diborylated congener **1** resulted in a complex mixture. Because we could not isolate the desired tetrameric complex from the mixture, we subjected the mixture to a subsequent reductive elimination reaction with PPh_3. After purification with silica gel and gel permeation chromatography, we obtained the target [4]cyclo-3,9-chrysenylene ($[4]CC_{3,9}$) in 8% yield (Scheme 1). Unlike the case with [4]cyclo-2,8-chrysenylene ($[4]CC_{2,8}$) that yielded a mixture of four diastereomers comprising two helical and two armchair models,[8] $[4]CC_{3,9}$ was obtained as a single diastereomer.

The possible structures of $[4]CC_{3,9}$ are described because the belt persistence of [4]CC gives rise to a unique atropisomerism and hence stereoisomers.[9] Depending on the orientations of the chrysenylene units in the nanotube, there are six possible structures for $[4]CC_{3,9}$: two sets of enantiomers and two other diastereomers. The four diastereomeric structures can be discriminated by the stereoconfigurations at the arylene linkages, the chiral indexes, and the point symmetry as $(E,E,E,E)/(16,0)/D_4$, $(E,E,Z,Z)/(12,4)/C_2$, $(E,Z,E,Z)/(8,8)_{AABB}/C_{2h}$, and $(Z,Z,Z,Z)/(8,8)_{ABAB}/D_{4d}$, respectively (Figure 1). The enantiomeric relationship, originating solely from the topology of the chrysenylene units, can be found in the zigzag and helical models (i.e., D_4-(16,0)- and C_2-(12,4)-$[4]CC_{3,9}$) because of their chiral arrangement of the sp^2-carbon networks.

The single diasteromeric structure of the isolated $[4]CC_{3,9}$ was successfully identified through spectroscopic and chromatographic analysis. In the characteristic aromatic region of NMR spectra, we observed four signals for ^1H and nine signals for ^{13}C (Figures 2a and S2), which narrowed the list of possible structures to two: either D_4-(16,0) or D_{4d}-$(8,8)_{ABAB}$. We then subjected the compound to HPLC analysis with chiral, cholesterylated silica gel columns and found two separate peaks in the chromatograms (Figure 2b). The observation of CD-active peaks with opposite, that is, negative and positive, signs showed that they are optically active enantiomers and that the compound is the finite zigzag SWNT, i.e., (16,0)-$[4]CC_{3,9}$

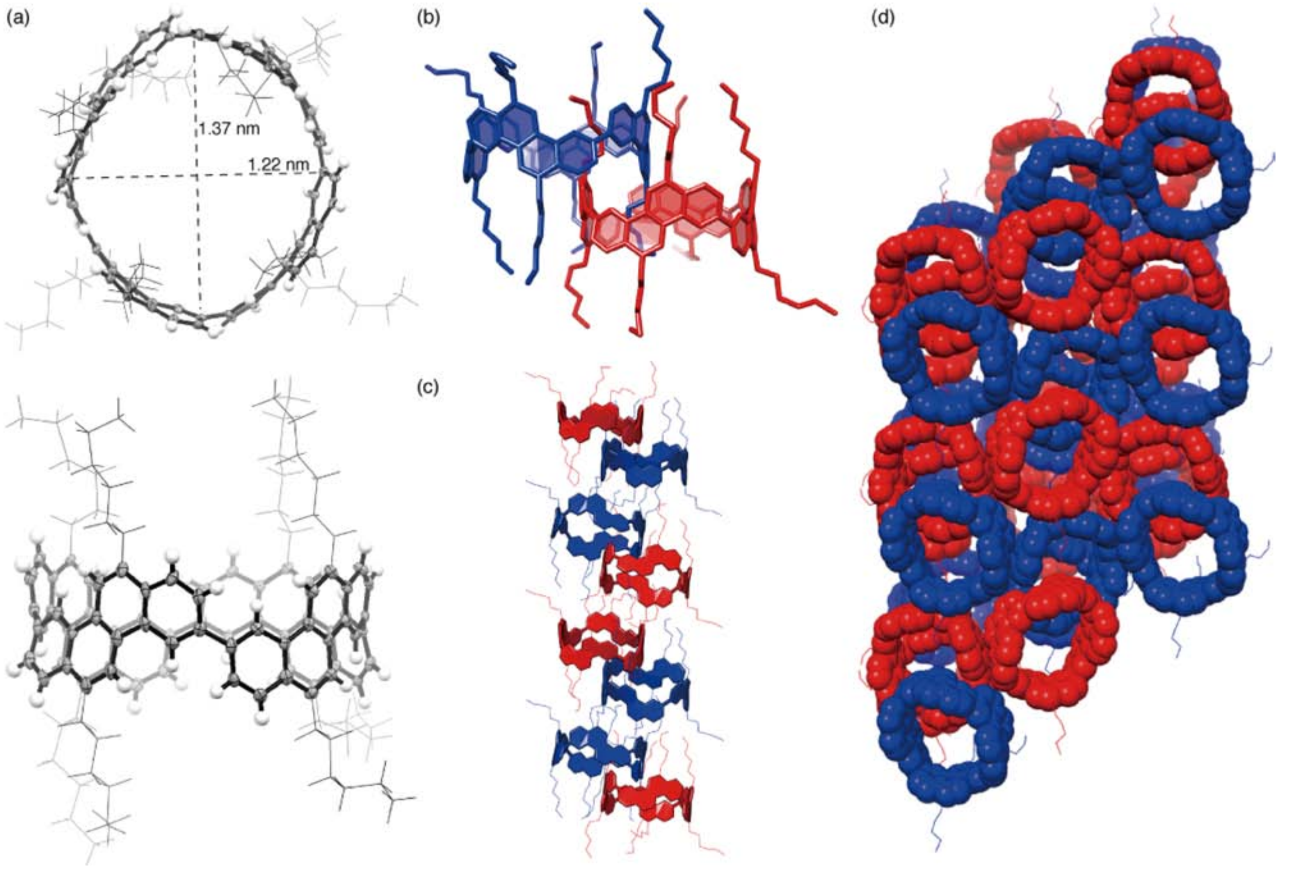


Figure 3. Molecular and packing structures of (16,0)-[4]$CC_{3,9}$. (a) Molecular structures of (+)-(16,0)-[4]$CC_{3,9}$. Hexyl substituents are shown in wireframe diagrams, and chrysenylenes are shown in ORTEP diagrams with thermal ellipsoids at the 50% level. A top view along the cylindrical axis and a side view along the minor oval axis are shown. (b) An interwoven pair of enantiomers viewed from side. (c) Columnar array of the paired enantiomers. The pairs are alternately stacked, and four pairs are shown. (d) Packing structure of the columns viewed along the columnar direction. For b−d, (+)- and (−)-isomers were colored in red and blue, respectively, and hydrogen atoms were omitted for clarity. See Figure S3 for details of the intermolecular contacts.

with D_4 symmetry. Note that this result demonstrates that the zigzag SWNT structures are synthetically accessible with cycloarylene molecules, although reactive open-shell cyclacene molecules have been sought for the models.[3,10,11] The isolation of each enantiomer was successful using the larger cholesterylated silica gel columns, and the spectroscopic analysis confirmed the enantiomeric relationship (Figure 2c and S6; The accompanying absorption spectra are shown in Figure S7.). Due to its unprecedented structure, no appropriate descriptors for the absolute configurations are available to discriminate these topological isomers, and we tentatively used (+)- and (−)-descriptors from the CD peaks at 420 nm (Figure 2d). A theoretical study showed that the (16,0)-[4]$CC_{3,9}$ is the most stable among four diastereomers (see Supplementary Methods), which may be one of the key factors in the selective production.

The structure of the zigzag nanotube was further confirmed by X-ray crystallographic analysis of a single crystal that unexpectedly showed a packing structure suggestive of the molecular design of nanotube assembly. After purification with silica gel column chromatography, the crystals were grown from the racemic mixture of (16,0)-[4]$CC_{3,9}$ in methanol/CH_2Cl_2. The molecular structures are shown in Figure 3, and the representative intermolecular contacts are shown in Figure S3. The tubular structure was slightly distorted in the radial direction to form an oval-shaped nanotube with a 1.37-nm major axis and 1.22-nm minor axis (Figure 3a). Eight hexyl substituents at 6,12-positions of chrysenylene units were located at the zigzag open end of the nanotube and stood mainly along the cylindrical axis. Interestingly, these hexyl substituents helped to weave the columnar array of the racemate in the crystal packing. Thus, the enantiomers were entangled in a thread-in-bead manner to form an interwoven pair in a unit cell (Figure 3b). The interwoven pairs further accommodated the methylene chains of other pairs in the remaining void space of the tube to result in a columnar array of the molecules (Figure 3c). The CH−π interactions between the methylene “thread” and the nanotube “bead” may not be strong,[14,15] and the assembly may be driven primarily by the entropic gain upon packing.[16] The columns were further bundled in a hexagonal manner in the presence of the CH−π and π−π contacts (Figures 3d and S3). The single crystals of the X-ray quality was obtained relatively easily from [4]$CC_{3,9}$ but not from [4]$CC_{2,8}$, which may indicate favorable assistance from the methylene chains along the cylindrical axis for the crystal growth.

The isolation of (16,0)-[4]$CC_{3,9}$ enantiomers implies the presence of strain-induced atropisomerism,[9] and we revealed an extreme rotational restriction at the single-bond linkages to maintain the tubular shape of the molecule. Previously, we succeeded in estimating the energy barrier of 26 kcal/mol for the rotation of chrysenylene units in [4]$CC_{2,8}$ by following the thermal isomerization processes from the (*P*)-(12,8)-isomer with HPLC analysis.[9] Following this example, we attempted to trace the isomerization of (−)-(16,0)-[4]$CC_{3,9}$ with HPLC analysis. However, even after heating the solution of the (−)-isomer for 1440 h at 200 °C, we did not observe the enantiomeric (+)-isomer (Figure S4).[17] The absence of the isomerization of [4]$CC_{3,9}$ at 200 °C for several hundreds of hours was in stark contrast to the case of [4]$CC_{2,8}$, where the half-life of one isomer was estimated to be 2 s at 180 °C.[9] Moreover, the barrier of single-bond rotation of [4]$CC_{3,9}$ is so large that it even surpassed that of a C−C double bond with a low energy barrier (40 kcal/mol), for which a half-life of 58 h at 200 °C was indicated.[18] Such a strong constraint at the single-bond linkages shows that (16,0)-[4]$CC_{3,9}$ possesses an extremely persistent tubular shape that is one of the characteristic structural features of SWNT. Mechanistically, the isomerization of the nanohoop accompanies a concave−convex conversion of the rotating arylene panel, and, consequently, a flattened transition geometry.[9] Although we could not locate the transition structure for [4]$CC_{3,9}$ isomerization by theoretical analysis, we can surely expect a more severe distortion for the 3,9-linked cyclochrysenylene as we see the highly distorted hoop in the line diagram (Figure S5). Our observation suggested that topological and geometrical consideration of the molecular structures is important for the rational design of nanocarbon models.[19]

With the present synthesis of a zigzag SWNT model, we have completed the bottom-up synthesis of all three types of belt-persistent SWNT models with the identical chemical composition ($C_{120}H_{136}$). The present study showed that simple but logical approaches are valid for the synthesis of finite SWNT and yet to be explored in this new research field. Comparison of the properties of these “SWNT isomers” is of great interest to explore the fundamental structural chemistry of nanotubes in the future. This study also demonstrated that devising the cutout positions allows the synthesis of isolable finite structures from the reactive open-shell structures of zigzag SWNT[10] and may further stimulate the nanotube synthesis to be explored through imaginative target settings along with the logical retrosynthetic analysis.[20] The new packing motif revealed the possibility of thread-in-bead columnar assembly of tubular π-rich molecules and may be rationally extended to the molecular design of functional supramolecular polymeric or liquid-crystalline materials.[12,16,21,22]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Physical data of compounds and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

isobe@m.tohoku.ac.jp

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This study was partly supported by KAKENHI (24241036, 20108015) and the Asahi Glass Foundation. We thank Prof. N. Teramae (Tohoku Univ.) for the CD instrument, Prof. T. Iwamoto (Tohoku Univ.) for the X-ray instrument, JEOL for the DART MS instruments, and Central Glass Co. for the gift of hexafluoroisopropanol.

■ REFERENCES

(1) Saito, R.; Dresselhaus, G.; Dresselhaus, M. S. *Physical Properties of Carbon Nanotubes*; Imperial: London, 1998.

(2) Nakamura, E.; Tahara, K.; Matsuo, Y.; Sawamura, M. *J. Am. Chem. Soc.* **2003**, *125*, 2834−2835.

(3) Jasti, R.; Bertozzi, C. R. *Chem. Phys. Lett.* **2010**, *494*, 1−7.

(4) Jasti, R.; Bhattacharjee, J.; Neaton, J. B.; Bertozzi, C. R. *J. Am. Chem. Soc.* **2008**, *130*, 17646−17647. Takaba, H.; Omachi, H.; Yamamoto, Y.; Bouffard, J.; Itami, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 6112−6116.

(5) Yamago, S.; Watanabe, Y.; Iwamoto, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 757−759.

(6) Omachi, H.; Matsuura, S.; Segawa, Y.; Itami, K. *Angew. Chem., Int. Ed.* **2010**, *49*, 10202−10205. Iwamoto, T.; Watanabe, Y.; Sakamoto, Y.; Suzuki, T.; Yamago, S. *J. Am. Chem. Soc.* **2011**, *133*, 8354−8361. Segawa, Y.; Miyamoto, S.; Omachi, H.; Matsuura, S.; Šenel, P.; Sasamori, T.; Tokitoh, N.; Itami, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 3244−3248. Segawa, Y.; Šenel, P.; Matsuura, S.; Omachi, H.; Itami, K. *Chem. Lett.* **2011**, *40*, 423−425. Sisto, T. J.; Golder, M. R.; Hirst, E. S.; Jasti, R. *J. Am. Chem. Soc.* **2011**, *133*, 15800−15802. Xia, J.; Jasti, R. *Angew. Chem., Int. Ed.* **2012**, *51*, 2474−2476.

(7) Segawa, Y.; Omachi, H.; Itami, K. *Org. Lett.* **2010**, *12*, 2262−2265. Omachi, H.; Segawa, Y.; Itami, K. *Org. Lett.* **2011**, *13*, 2480−2483. Yagi, A.; Segawa, Y.; Itami, K. *J. Am. Chem. Soc.* **2012**, *134*, 2962−2965.

(8) Hitosugi, S.; Nakanishi, W.; Yamasaki, T.; Isobe, H. *Nat. Commun.* **2011**, *2*, doi: 10.1038/ncomms1505.

(9) Hitosugi, S.; Nakanishi, W.; Isobe, H. *Chem.—Asian J.* **2012**, *7*, 1550−1552.

(10) Chen, Z.; Jiang, D. -E.; Lu, X.; Bettinger, H. F.; Dai, S.; Schleyer, P. R.; Houk, K. N. *Org. Lett.* **2007**, *9*, 5449−5452.

(11) Tahara, K.; Tobe, Y. *Chem. Rev.* **2006**, *106*, 5274−5290.

(12) Niyogi, S.; Hamon, M. A.; Hu, H.; Zhao, B.; Bhowmik, P.; Sen, R.; Itkis, M. E.; Haddon, R. C. *Acc. Chem. Res.* **2002**, *35*, 1105−1113. Hirsch, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1853−1859.

(13) Isobe, H.; Hitosugi, S.; Matsuno, T.; Iwamoto, T.; Ichikawa, J. *Org. Lett.* **2009**, *11*, 4026−4028. Hitosugi, S.; Nakamura, Y.; Matsuno, T.; Nakanishi, W.; Isobe, H. *Tetrahedron Lett.* **2012**, *53*, 1180−1182.

(14) Nishio, M. *CrystEngComm* **2004**, *6*, 130−158. Meyer, E. A.; Castellano, R. K.; Diederich, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 1210−1250.

(15) Koshino, M.; Tanaka, T.; Solin, N.; Suenaga, K.; Isobe, H.; Nakamura, E. *Science* **2007**, *316*, 853. Koshino, M.; Solin, N.; Tanaka, T.; Isobe, H.; Nakamura, E. *Nat. Nanotechnol.* **2008**, *3*, 595−597.

(16) Ciferri, A. *Liq. Cryst.* **1999**, *26*, 489−494. Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071−4097.

(17) Although there appeared small peaks in the HPLC analysis after 1440 h, we could not identify the structure due to the minute amount of the compounds.

(18) Eliel, E. L.; Willen, S. H. In *Stereochemistry of Organic Compounds*; Wiley: New York, 1994; Chapter 9.

(19) Nakanishi, W.; Yoshioka, T.; Taka, H.; Xue, J. Y.; Kita, H.; Isobe, H. *Angew. Chem., Int. Ed.* **2011**, *50*, 5323−5326. Nakanishi, W.; Matsuno, T.; Ichikawa, J.; Isobe, H. *Angew. Chem., Int. Ed.* **2011**, *50*, 6048−6051.

(20) Corey, E. J; Chen, X. -M. *The Logic of Chemical Synthesis*; Wiley: New York, 1995.

(21) Aida, T.; Meijer, E. W.; Stupp, S. I. *Science* **2012**, *335*, 813−817.

(22) Mitsuhashi, R.; Suzuki, Y.; Yamanari, Y.; Mitamura, H.; Kambe, T.; Ikeda, N.; Okamoto, H.; Fujiwara, A.; Yamaji, M.; Kawasaki, N.; Maniwa, Y.; Kubozono, Y. *Nature* **2010**, *464*, 76−79.