# Thermotropic Columnar Liquid Crystal of a $C_6$-Symmetric Hydrogen-bonded Hexakis(phenylethynyl)benzene Derivative with Amino Acid Pendant Groups

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The thermotropic liquid crystalline $C_6$-symmetric hydrogen-bonded disk-like molecule has been obtained in a hexakis(phenylethynyl)benzene derivative bearing chiral didodecyl L-glutamates, which forms a hexagonal columnar phase over a wide temperature range including room temperature, where each $\pi$–$\pi$ stacking between the large central cores is reinforced by the six intermolecular hydrogen bonds.

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Supramolecular chiral assemblies constructed using various types of noncovalent bonding interaction, as utilized in biological systems, are of great interest from fundamental and biological viewpoints and offer potential applications in functional materials exhibiting liquid crystal (LC), charge transport, luminescence, and other combined properties.[1] Among such supramolecular assemblies, most of the ordered structures have been obtained from disk-shaped molecules, which offer the possibility of forming highly ordered columnar (Col) LC.[2] To stabilize the $\pi$–$\pi$ stacking among aromatic groups and reinforce the intracolumnar stacking order, it is important to enlarge the disk size[3] and/or to introduce hydrogen bonds.[3d,4] The majority of studies on hydrogen-bonded helical columns have been performed on 1,3,5-benzene tricarboxamide derivatives, which are $C_3$-symmetric molecules consisting of a central benzene ring and three peripheral chiral segments connected via amide bonds.[3f,3g,5] In this system, the $\pi$–$\pi$ interactions of the central benzene cores are assisted by three fold intermolecular hydrogen bonding. Amino acid units are also widely used as effective structuring elements which form hydrogen bonds in self-assembled architectures such as liquid crystalline dendritic peptides.[6] From this background, we previously designed a $C_6$-symmetric hydrogen-bonded disk-like molecule, L-**1**, and succeeded in further enhancing the stability of the supramolecular helical columnar structure (Figure 1).[7] The L-**1** compound consists of a large hexakis(phenylethynyl)benzene central core bearing chiral L-alanine parts and peripheral hydrophobic dodecyl chains. The stacking among large central cores of L-**1** is enforced by six intermolecular hydrogen bonds, leading to an exceptionally stable supramolecular helical columnar structure, which is maintained even at 100 °C in dilute *n*-alkane solutions. The rigidity of the helical column also produced lyotropic LC properties at a relatively low concentration, ca. 6 wt % in *n*-alkane but not a thermotropic LC. The LC formation in *n*-alkane suggests a possibility of forming a thermotropic LC if density of alkyl chains is increased. Hence, in the present study, we synthesized an analogous compound, L-**2**, bearing chiral didodecyl L-glutamate (Figure 1).

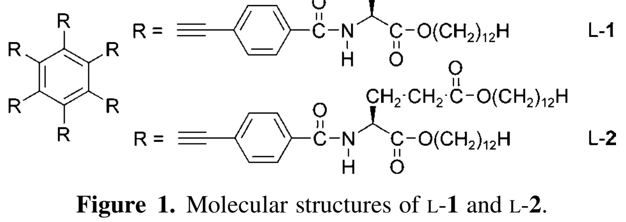

**Figure 1.** Molecular structures of L-**1** and L-**2**.

First of all, the self-assembly of L-**2** was confirmed by measuring UV–visible absorption (UV–vis) and circular dichroism (CD) spectra in *n*-heptane ($4.20 \times 10^{-5}$ M) at 25 °C (Figure S1).[8] L-**2** shows clear Cotton effects and the spectral features are similar to those of the analogous L-**1** reported previously.[7] This result indicates that L-**2** also forms a supramolecular helical columnar structure even in such a dilute solution. Moreover, in the drying process of this solution, L-**2** exhibits a lyotropic LC. This fact further supports that columnar structure is being constructed.[3g,5c,7]

The thermal behavior of L-**2** in the bulk state was investigated by differential scanning calorimetry and polarizing microscopy (Figures S2a and S2b, respectively).[8] The combined results revealed that L-**2** forms a Col LC phase in a wide temperature range from ca. 0 to ca. 170 °C, where a dendritic growth texture is visible (Figure S2b).[8]

To get information about the molecular aggregation state such as the peripheral alkyl chain motion and the hydrogen bonding, temperature-dependent infrared (IR) spectra were measured on the second heating. Figure S3 shows representative IR spectra of L-**2**.[8] The methylene C–H antisymmetric ($\nu_{as}(CH_2)$) and symmetric ($\nu_s(CH_2)$) frequencies of L-**2** are observed at 2924 (at 30–180 °C) and 2853 (at 30 °C)–2855 $cm^{-1}$ (180 °C), respectively, and these two bands are almost independent of temperature. The values indicate that the conformational structure of the alkyl chains is liquid-like in the Col LC state.[9] Information about the hydrogen-bonding state was obtained from the N–H stretching (amide A) and the C=O stretching vibrations (amide I).[5b,5e] At 30 °C in the Col LC state, the vibrations of amide A and amide I are observed at 3264 and 1633 $cm^{-1}$, respectively, indicating the presence of a strong hydrogen bonding within the column formed by L-**2**. When temperature is elevated from 30 to 165 °C in the Col LC state, both amide A and amide I bands are gradually shifted to the higher wavenumbers, 3300 and 1642 $cm^{-1}$, respectively (Figure 2). This result indicates that the hydrogen bonding within the column is maintained over the whole temperature range of the Col LC state but gradually weakened as a result of thermal motion. The significant changes of these two amide bands are observed at the LC–Iso (isotropic liquid state) transition temperature, 170 °C, where the vibrations of both amide A and amide I bands change drastically to the much higher wavenumbers, 3336 and 1671 $cm^{-1}$, respectively. These changes imply that the hydrogen bonding within the column is broken upon the LC–Iso transition.

The liquid crystalline structure was investigated by X-ray diffraction (XRD) measurements (Figure 3). In the temperature range from 30 to 165 °C of the Col LC state, several sharp reflec-

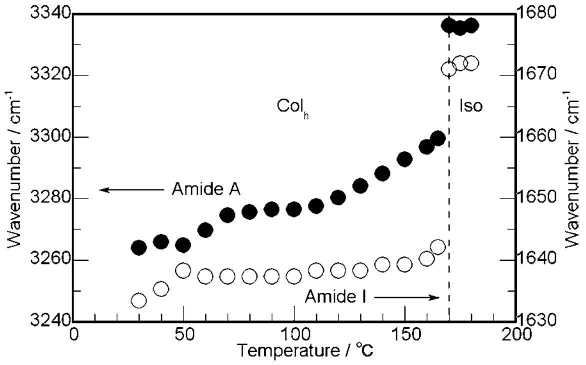

**Figure 2.** Temperature dependence of the peak positions of the amide A (closed circles) and the amide I (open circles) bands for L-**2**.

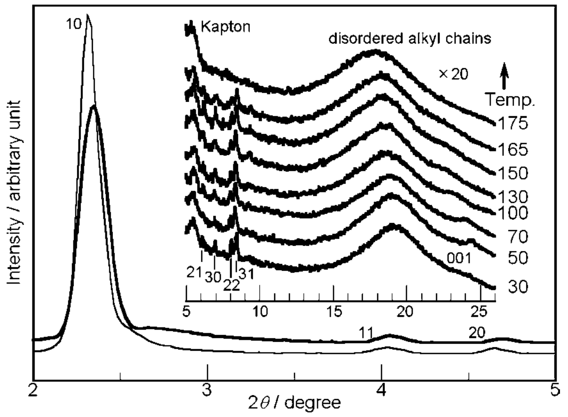

**Figure 3.** XRD profiles ($2\theta = 2$–$5°$) of L-**2** measured at 30 (thin line) and 165 °C (bold line). The inset shows the temperature-dependent XRD profiles ($2\theta = 5$–$26°$).

tions and a broad scattering ($2\theta \approx 19°$) with a shoulder ($2\theta \approx 24°$) are observed in the small-angle region and the wide-angle region, respectively. The sharp reflections and the shoulder peak disappear at 175 °C in the Iso state. This change of the XRD profiles and the IR result mentioned above indicate that the broad peak is attributed to a disordered conformation of the peripheral alkyl chains ($d_{\mathrm{al}}$) and the shoulder peak is related to the average $\pi$–$\pi$ stacking, namely, intracolumnar distance ($d_{001}$) between large hexakis(phenylethynyl)benzene cores. The reflections in the small-angle region were analyzed for the XRD pattern observed at 30 °C. These peaks are indexed as $hk$ reflections ($h, k$ = integer) of a hexagonal columnar (Col$_{\mathrm{h}}$) phase with a lattice parameter of $a = 4.382$ nm (corresponding to the intercolumnar distance), and the spacing data including the values of $d_{001}$ (0.37 nm) and $d_{\mathrm{al}}$ (0.47 nm) are summarized in Table S1.[8] Here, the density calculated on this basis, 1.01 g cm$^{-3}$, is also reasonable. The temperature dependence of the XRD profiles revealed no LC structural variation in the temperature range of the Col LC state, but only a slight compression of the intercolumnar distance and an expansion of the intracolumnar distance were observed for the increased temperature from 30 to 165 °C; the values of $a$ and $d_{001}$ at 165 °C were 4.343 and ca. 0.39 nm, respectively. The calculated linear thermal expansion coefficients were extremely small ($-6.62 \times 10^{-5}$ K$^{-1}$) for the intercolumnar spacing and relatively large (ca. $4.0 \times 10^{-4}$ K$^{-1}$) for the intracolumnar distance. This implies that in the Col$_{\mathrm{h}}$ LC state, the closed packing among the columns (lateral two-dimensional order) is substantially maintained but the intracolumnar distance is gradually increased with a decrease of stacking interactions originated from weakening of intermolecular hydrogen bonding.

In summary, we have found the first example of a $C_6$-symmetric hydrogen-bonded disk-like molecule, L-**2**, exhibiting a thermotropic LC. The $\pi$–$\pi$ stacking between large central cores of L-**2** is reinforced by six intermolecular hydrogen bonds, leading to an ordered Col$_{\mathrm{h}}$ LC formation over a wide temperature range including room temperature.

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### References and Notes

1 a) *Top. Stereochem.* **2003**, *24*. b) *Top. Curr. Chem.* **2006**, *265*. c) *Struct. Bonding (Berlin)* **2008**, *128*.

2 S. Laschat, A. Baro, N. Steinke, F. Giesselmann, C. Hägele, G. Scalia, R. Judele, E. Kapatsina, S. Sauer, A. Schreivogel, M. Tosoni, *Angew. Chem., Int. Ed.* **2007**, *46*, 4832.

3 a) Ž. Tomović, M. D. Watson, K. Müllen, *Angew. Chem., Int. Ed.* **2004**, *43*, 755. b) S. Saïdi-Besbes, É. Grelet, H. Bock, *Angew. Chem., Int. Ed.* **2006**, *45*, 1783. c) Ž. Tomović, J. van Dongen, S. J. George, H. Xu, W. Pisula, P. Leclère, M. M. J. Smulders, S. De Feyter, E. W. Meijer, A. P. H. J. Schenning, *J. Am. Chem. Soc.* **2007**, *129*, 16190. d) X. Dou, W. Pisula, J. Wu, G. J. Bodwell, K. Müllen, *Chem.—Eur. J.* **2008**, *14*, 240. e) X. Feng, V. Marcon, W. Pisula, M. R. Hansen, J. Kirkpatrick, F. Grozema, D. Andrienko, K. Kremer, K. Müllen, *Nat. Mater.* **2009**, *8*, 421. f) A. R. A. Palmans, J. A. J. M. Vekemans, H. Fischer, R. A. Hikmet, E. W. Meijer, *Chem.—Eur. J.* **1997**, *3*, 300. g) A. R. A. Palmans, J. A. J. M. Vekemans, R. A. Hikmet, H. Fischer, E. W. Meijer, *Adv. Mater.* **1998**, *10*, 873. h) C. V. Yelamaggad, A. S. Achalkumar, D. S. S. Rao, S. K. Prasad, *J. Mater. Chem.* **2007**, *17*, 4521.

4 a) R. I. Gearba, M. Lehmann, J. Levin, D. A. Ivanov, M. H. J. Koch, J. Barberá, M. G. Debije, J. Piris, Y. H. Geerts, *Adv. Mater.* **2003**, *15*, 1614. b) M. Palma, J. Levin, O. Debever, Y. Geerts, M. Lehmann, P. Samorì, *Soft Matter* **2008**, *4*, 303.

5 a) M. P. Lightfoot, F. S. Mair, R. G. Pritchard, J. E. Warren, *Chem. Commun.* **1999**, 1945. b) M. L. Bushey, A. Hwang, P. W. Stephens, C. Nuckolls, *J. Am. Chem. Soc.* **2001**, *123*, 8157. c) M. L. Bushey, A. Hwang, P. W. Stephens, C. Nuckolls, *Angew. Chem., Int. Ed.* **2002**, *41*, 2828. d) K. P. van den Hout, R. Martín-Rapún, J. A. J. M. Vekemans, E. W. Meijer, *Chem.—Eur. J.* **2007**, *13*, 8111. e) I. Paraschiv, K. de Lange, M. Giesbers, B. van Lagen, F. C. Grozema, R. D. Abellon, L. D. A. Siebbeles, E. J. R. Sudhölter, H. Zuilhof, A. T. M. Marcelis, *J. Mater. Chem.* **2008**, *18*, 5475. f) P. J. M. Stals, M. M. J. Smulders, R. Martín-Rapún, A. R. A. Palmans, E. W. Meijer, *Chem.—Eur. J.* **2009**, *15*, 2071.

6 a) V. Percec, A. E. Dulcey, V. S. K. Balagurusamy, Y. Miura, J. Smidrkal, M. Peterca, S. Nummelin, U. Edlund, S. D. Hudson, P. A. Heiney, H. Duan, S. N. Magonov, S. A. Vinogradov, *Nature* **2004**, *430*, 764. b) Y. Kamikawa, M. Nishii, T. Kato, *Chem.—Eur. J.* **2004**, *10*, 5942.

7 K. Sakajiri, T. Sugisaki, K. Moriya, *Chem. Commun.* **2008**, 3447.

8 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

9 Y. Xu, S. Leng, C. Xue, R. Sun, J. Pan, J. Ford, S. Jin, *Angew. Chem., Int. Ed.* **2007**, *46*, 3896.

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