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Headline Articles

Copper(I) Ion Mediated Self-Assembly of Triple-Stranded Helicates from Oligo(2-ethynylpyridines): Synthesis, Structure, and Properties

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The reaction of oligo(2-ethynylpyridines) (**L1**–**L8**) with copper(I) ions proceeded smoothly to afford tri-, tetra-, and pentanuclear triple-stranded helicates (**CL1**–**CL8**) in good yields. If a chiral ligand was used, the stereoselective self-assembly of chiral helicates with one particular chirality was achieved in the solid state. Racemization of copper(I) helicates was also observed in solution.

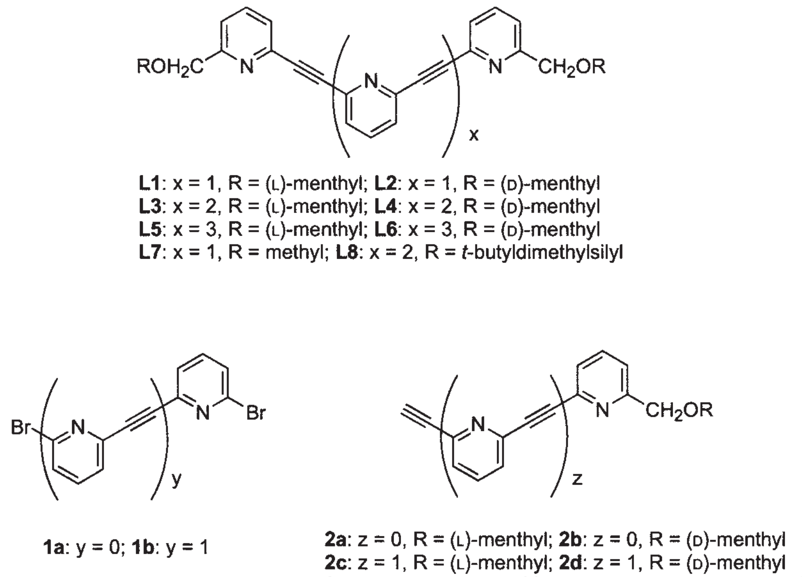
Metal ion assisted self-assembly of functionalized higher order supramolecular structures is currently of interest in the field of supramolecular chemistry.[1] Over the past decade, various reports have been published on the self-assembly of supramolecular helicates, which are discrete helical supramolecular complexes constituted by one or more covalent organic strands wrapped about and coordinated to a series of ions defining the helical axis, from polydentate nitrogen ligands and metal ions.[2] Among these polydentate nitrogen ligands, oligopyridines have been found to be one of the most versatile building blocks for the construction of supramolecular systems.[3] Ethynyl-bridged oligopyridines would especially be expected to provide us a facile entry into molecular wires based on transition metal complexes with π-conjugated ligands. In 1993, Potts and co-workers reported that unsubstituted 2,6-bis(2-pyridylethynyl)pyridine having three pyridine rings, which belongs a π-conjugated oligo(2-ethynylpyridine) system, could be treated with copper(I) ions to yield a unique trinuclear triple-stranded helicate.[4a] However, the stereoselective self-assembly of the copper(I) helicate and its detailed behavior in solution remain unsolved. Additionally, no oligo(2-ethynylpyridines) having more than four pyridine rings have been documented in the literature to date,[4b–d] although there have been many reports on the acetylenic-bridged oligo(bi- or terpyridines)[5] and the simple 2-ethynylpyridines such as bis(2-pyridyl)acetylenes.[6] Since supramolecular helicates are intrinsically chiral, the self-assembly of helicates from achiral ligands and labile metal centers yields racemic mixtures of right-handed (plus, *P*) and left-handed (minus, *M*) helicates. Various procedures for their resolution have been successfully applied in order to obtain the pure enantiomers. The introduction of a chiral substituent into the backbone of the ligands is one effective method for the stereoselective synthesis of helicates with one particular chirality.[7]

Recently, we reported that the coordination of 1,2-bis(2-pyridylethynyl)benzenes with metal ions provided planar chelate complexes[8] or molecular rectangular boxes.[9] Furthermore, we have also reported a facile synthesis of a series of oligo(2-ethynylpyridines) with three, four, five, and six pyridine rings.[10] We expected that the stereoselective self-assembly of supramolecular helicates would be achieved by using oligo(2-ethynylpyridines) bearing a chiral substituent, and that the behavior of the supramolecular helicates in solution would be clarified. In this paper, we describe the syntheses and copper(I) ion mediated self-assembly of the chiral oligo(2-ethynylpyridines), **L1**–**L6**, along with the corresponding achiral ones, **L7** and **L8** (Chart 1). The solution properties of copper(I) helicates are also reported.

Results and Discussion

Preparation of Oligo(2-ethynylpyridines) L1–L8. Dibromopyridines (**1**) and 2-ethynylpyridines (**2**) are key intermediates for the synthesis of oligo(2-ethynylpyridines). The synthesis of bis(6-bromo-2-pyridyl)acetylene (**1b**) is shown in Scheme 1. Treatment of 2-bromo-6-(hydroxymethyl)pyridine (**3**),[11,12] which was prepared from commercially available 2,6-dibromopyridine (**1a**), with methanesulfonyl chloride (MsCl) in tetrahydrofuran (THF) at −40 °C, followed by displacement of the resulting mesylate with iodide ion in acetone at 60 °C, gave the corresponding primary iodide (**4**) in 93% yield from **3**. Arbuzov reaction of **4** with triethyl phosphite at 150 °C gave the phosphonate (**5**) in quantitative yield. Subjection of 2-bromo-6-formylpyridine, which was prepared by oxidation of **3** with 1-iodylbenzoic acid (IBX)[13] in dimethyl sulfoxide (DMSO) at room temperature, to a Horner-Wadsworth-Emmons reaction with the sodium salt of **5** in THF at room temperature afforded exclusively *trans*-disubstituted ethylene derivative (**6**) in 92% yield. Bromination of **6** with bromine in chloroform at room temperature gave the tetrabromide (**7**) in 92% yield. Dehydrobromination of **7** with potassium *t*-butoxide at room temperature yielded the desired bis(6-bromo-2-pyridyl)acetylene (**1b**) in 90% yield.

The synthesis of other key intermediates (**2a–f**) is shown in

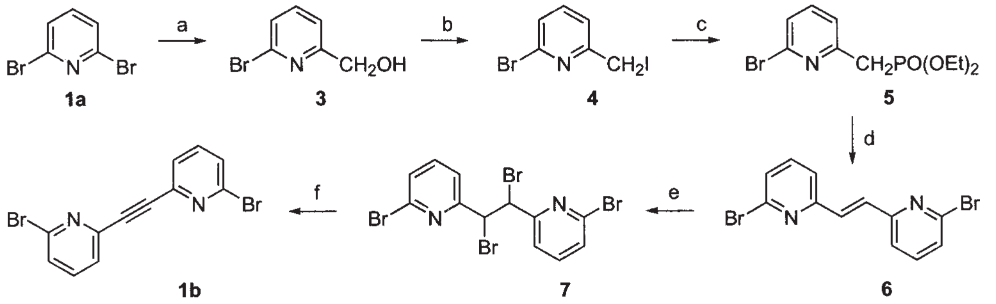


L1: x = 1, R = (L)-menthyl; **L2**: x = 1, R = (D)-menthyl
L3: x = 2, R = (L)-menthyl; **L4**: x = 2, R = (D)-menthyl
L5: x = 3, R = (L)-menthyl; **L6**: x = 3, R = (D)-menthyl
L7: x = 1, R = methyl; **L8**: x = 2, R = *t*-butyldimethylsilyl

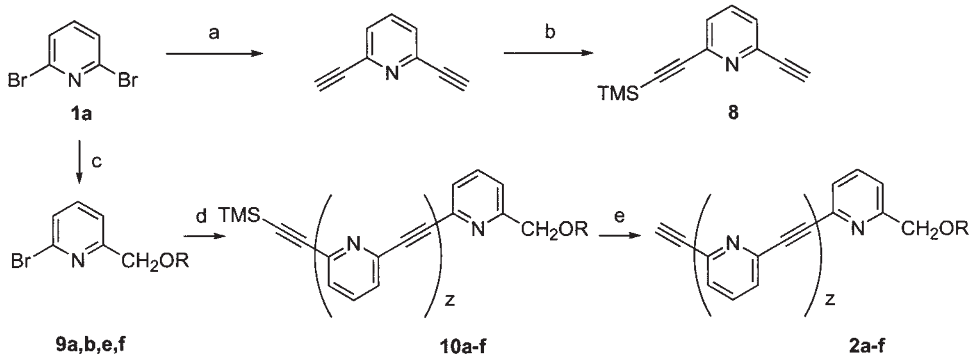
1a: y = 0; **1b**: y = 1

2a: z = 0, R = (L)-menthyl; **2b**: z = 0, R = (D)-menthyl
2c: z = 1, R = (L)-menthyl; **2d**: z = 1, R = (D)-menthyl
2e: z = 0, R = methyl; **2f**: z = 0, R = *t*-butyldimethylsilyl

Chart 1.



Scheme 1. Preparation of bis(6-bromo-2-pyridyl)acetylene (**1b**). *Reagents and conditions*: (a) (1) *n*-BuLi, THF, −78 °C, (2) DMF, THF, −78 °C, (3) $NaBH_4$, THF, 0 °C. (b) (1) MsCl, Et_3N, DMAP, THF, −40 °C, (2) NaI, acetone, 60 °C. (c) $P(OEt)_3$, 150 °C. (d) (1) NaH, THF, rt, (2) 2-bromo-6-formylpyridine, THF, rt. (e) Br_2, $CHCl_3$, rt. (f) *t*-BuOK, THF, rt.

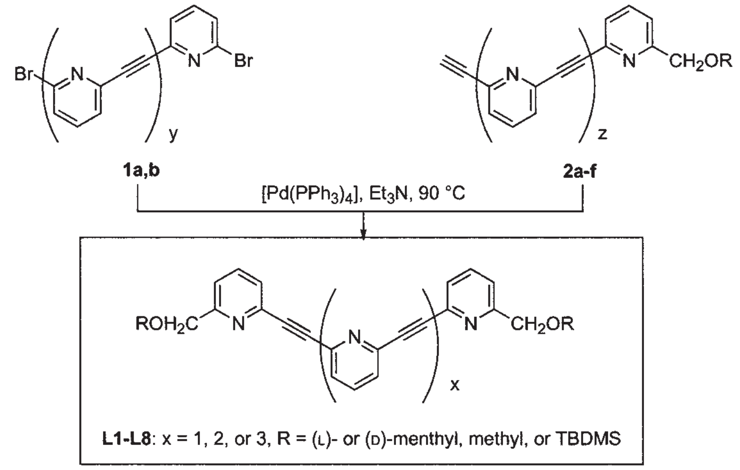


a: z = 0, R = (L)-menthyl; **b**: z = 0, R = R = (D)-menthyl, **c**: z = 1, R = (L)-menthyl
d: z = 1, R = (D)-menthyl, **e**: z = 0, R = methyl; **f**: z = 0, R = *t*-butyldimethylsilyl

Scheme 2. Preparation of ethynylpyridines (**2a**–**f**). *Reagents and conditions*: (a) (1) TMSA, $[PdCl_2(PPh_3)_2]$, CuI, Et_2NH, rt, (2) TBAF, THF, rt. (b) (1) EtMgBr, THF, rt, (2) TMSCl, rt. (c) see refs. 8, 9, and 13. (d) TMSA or compound **8**, $[Pd(PPh_3)_4]$, Et_2NH, 60 °C. (e) KOH, MeOH, 0 °C.

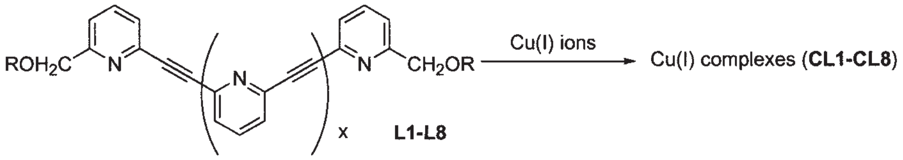
Scheme 2. 2,6-Bis(ethynyl)pyridine, which was prepared from **1a** according to the literature procedure,[14] was converted into mono TMS-ethynyl substituted pyridine (**8**) by treatment with ethylmagnesium bromide, followed by mono-silylation with trimethylsilyl chloride (TMSCl) in THF at room temperature in 64% yield. The cross-coupling reaction of the bromopyridine derivatives **9a**,[9] **9b**,[9] **9e**,[8,12] and **9f**[12] with (trimethylsilyl)acetylene (TMSA) or compound **8** in the presence of a catalytic amount of

Table 1. Synthesis of Oligo(2-ethynylpyridines) (**L1**–**L8**)



Entry	Compounds **1**	Compounds **2**	R	Products	Yield/%[a)]
1	**1a**	**2a**	(L)-menthyl	**L1** (x = 1)	92
2	**1a**	**2b**	(D)-menthyl	**L2** (x = 1)	90
3	**1b**	**2a**	(L)-menthyl	**L3** (x = 2)	86
4	**1b**	**2b**	(D)-menthyl	**L4** (x = 2)	86
5	**1a**	**2c**	(L)-menthyl	**L5** (x = 3)	75
6	**1a**	**2d**	(D)-menthyl	**L6** (x = 3)	72
7	**1a**	**2e**	methyl	**L7** (x = 1)	93
8	**1b**	**2f**	TBDMS[b)]	**L8** (x = 2)	96

a) Isolated yield. b) *t*-Butyldimethylsilyl.



CL1: $[Cu_3(\mathbf{L1})_3](PF_6)_3$; **CL2**: $[Cu_3(\mathbf{L2})_3](PF_6)_3$; **CL3**: $[Cu_4(\mathbf{L3})_3](BF_4)_4$; **CL4**: $[Cu_4(\mathbf{L4})_3](BF_4)_4$
CL5: $[Cu_5(\mathbf{L5})_3](BF_4)_5$; **CL6**: $[Cu_5(\mathbf{L6})_3](BF_4)_5$; **CL7**: $[Cu_3(\mathbf{L7})_3](PF_6)_3$; **CL8**: $[Cu_4(\mathbf{L8})_3](BF_4)_4$.

Scheme 3. Synthesis of copper(I) complexes (**L1**–**L8**).

$[Pd(PPh_3)_4]$ in diethylamine at 60 °C gave the corresponding TMS-protected derivatives (**10a**–**f**) in 83–99% yields. Cleavage of the silyl group with potassium hydroxide (KOH) in methanol at 0 °C afforded the desired products (**2a**–**f**) in 88–97% yields.

The synthesis of oligo(2-ethynylpyridines) (**L1**–**L8**) was achieved by the cross-coupling reaction of **1** with 2.3 equiv of **2** in the presence of a catalytic amount of $[Pd(PPh_3)_4]$ in diethylamine at 90 °C (Table 1). No racemization of the chiral centers took place under the conditions employed. The resulting ligands (**L1**–**L8**) were characterized by IR, UV, ^{1}H NMR, and ^{13}C NMR spectroscopies and by elemental analysis. All data were consistent with the proposed structures. A slight bathochromic shift with elongation of the conjugated systems was observed in the absorption spectra of the ligands in this study (λ_{max} 320 nm for **L1** (x = 1), 322 nm for **L3** (x = 2), 324 nm for **L5** (x = 3)). Furthermore, the ligands (**L1**–**L8**) were also found to emit fluorescence around 341–346 nm. Therefore, the π-conjugated framework of **L1**–**L8** should function as a novel fluorescent probe. Our synthetic methods are also of particular importance in that most of the compounds in this study were derived from only one starting material, 2,6-dibromopyridine (**1a**).

Self-Assembly of Copper(I) Helicates CL1–CL8. In the first place, we examined the coordination of the ligand (**L3**) with copper(I) ion. The reaction of **L3** with 1.4 equiv of $[Cu(CH_3CN)_4]BF_4$[15] in dichloromethane (CH_2Cl_2) at room temperature resulted in the immediate formation of yellow solutions, indicating a fast complexation with copper(I) ions, from which the desired copper(I) complex (**CL3**) was obtained as yellow blocks in 92% yield (Scheme 3). Elemental analysis of **CL3** showed the complex (**CL3**) to be $[Cu_4(\mathbf{L3})_3](BF_4)_4$. Electrospray ionization (ESI) mass spectrometry of an acetone solution of **CL3** did not show the parent peak of **CL3**; however, it showed average mass peaks at m/z 2671.0 for $[\mathbf{CL3}\text{-}(BF_4)]^+$ and 1292.1 for $[\mathbf{CL3}\text{-}(BF_4)_2]^{2+}$. These peaks were not observed by conventional techniques such as fast-atom bombardment (FAB) mass spectrometry. The measured isotopic patterns for these ions are in fair agreement with the calculated isotopic patterns. Examination of the isotopic abundance of the peak at m/z 1292.1 showed a peak separation of 0.5 units, which is typical of a doubly charged species, confirming the presence of the complex $[Cu_4(\mathbf{L3})_3](BF_4)_4$. The electronic spectra of **CL3** showed a new weakly broad absorption in 340–390 nm, which was assigned to a metal-to-ligand charge transfer band. Spectrophotometric titration of a CH_2Cl_2 solution of **L3** with a CH_2Cl_2 solution of $[Cu(CH_3CN)_4]BF_4$ gave clear isosbestic points, indicating that a single species was formed (Fig. 1). The change in absorbance analyzed by the mole ratio method at 350 nm showed a linear dependence on the amount of copper(I) salt added up to about 1:1.3 **L3**:copper(I) ratio (Fig. 2a). This result indicates that a $Cu_4(\mathbf{L3})_3$ composition is generated. The ^{1}H NMR spectra of the free ligand (**L3**) and of its copper(I) complex (**CL3**) are shown in Fig. 3. Upon metal complexation, specific signals of the ^{1}H NMR spectra undergo significant changes, which also make these signals key indicators of complexation. The signals of all the aromatic protons involved in **CL3** were shifted relative to those involved in **L3**. In particular, the proton signals (Hb and He) of the pyridine ring ($\Delta\delta = 0.21$) are shifted downfield relative to that of the free ligand (**L3**). The proton signals (Hc and Hd) of the pyridine ring ($\Delta\delta = -0.31$) are shifted upfield relative to that of **L3**. Other copper(I) complexes also exhibited similar behaviors in their spectrophotometric titration experiments and NMR spectroscopic studies. The reaction of **L4** or **L8** with $[Cu(CH_3CN)_4]BF_4$ in CH_2Cl_2 gave the desired copper(I) complexes (**CL4**: $[Cu_4(\mathbf{L4})_3](BF_4)_4$ or **CL8**: $[Cu_4(\mathbf{L8})_3](BF_4)_4$, respectively) as yellow blocks. The complexes (**CL3** and **CL4**) exhibited significant changes in the specific rotations: copper(I) complexes **CL3**, $[\alpha]_D$ −418 (*c* 0.96, CH_2Cl_2) for **L3**, $[\alpha]_D$ −60.2 (*c* 1.08, CH_2Cl_2); and **CL4**, $[\alpha]_D$ +422 (*c* 1.22, CH_2Cl_2) for **L4**, $[\alpha]_D$ +60.1 (*c* 1.15, CH_2Cl_2). Such results indicate that the reaction of the present ligands with

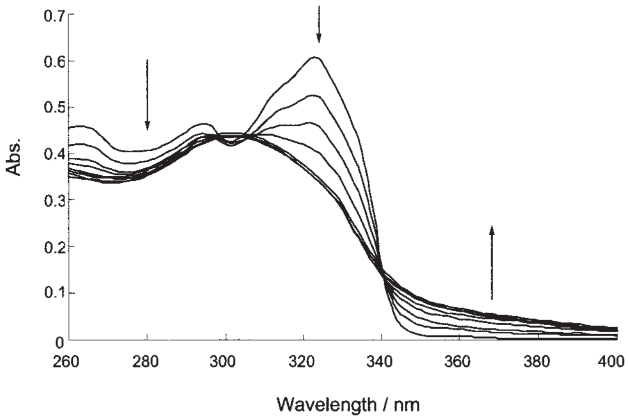


Fig. 1. Spectrophotometric titration of **L3** with $[Cu(CH_3CN)_4]BF_4$ in CH_2Cl_2.

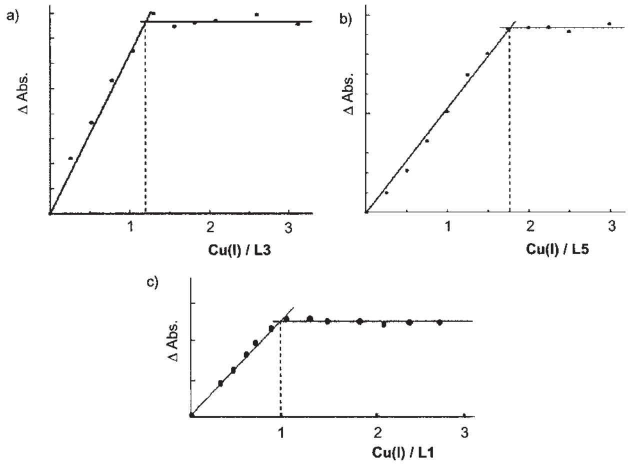


Fig. 2. The changes in absorbance analyzed by the mole ratio methods. a) Cu(I)/**L3** at 350 nm. b) Cu(I)/**L5** at 330 nm. c) Cu(I)/**L1** at 370 nm.

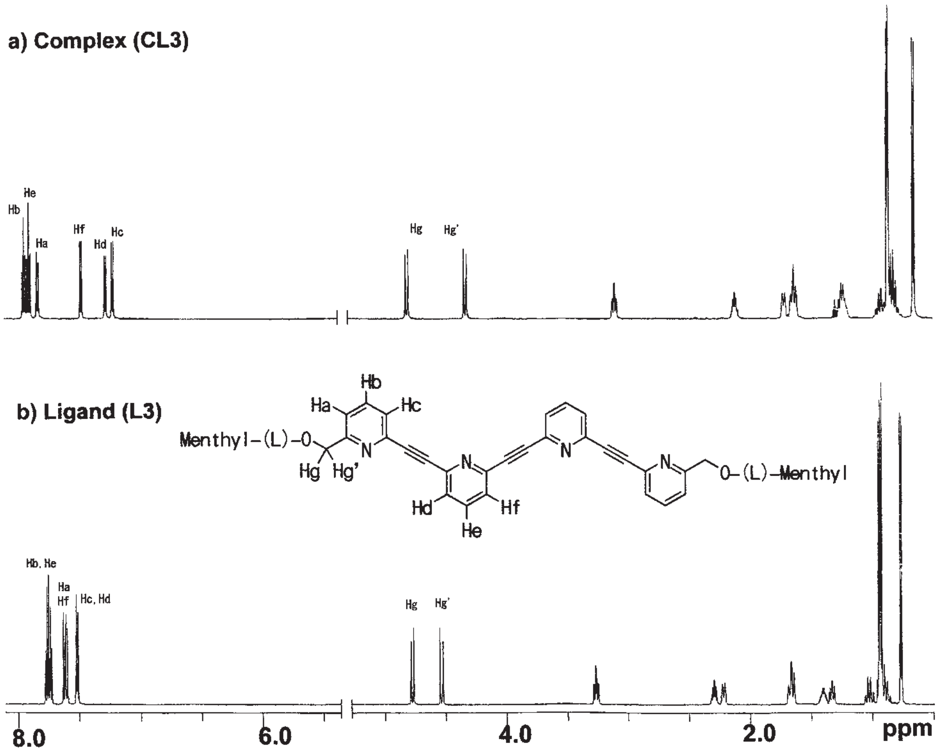


Fig. 3. ^{1}H NMR spectra (600 MHz, CD_2Cl_2) of (a) the copper(I) complex (**CL3**) and (b) the ligand (**L3**).

copper(I) salts proceeded stereoselectively to afford optical active copper(I) complexes. Similarly, the complex-forming reaction of **L1**, **L2**, or **L7** with an equimolar amount of $[Cu(CH_3CN)_4]PF_6$[16] in CH_2Cl_2 at room temperature gave the copper(I) complexes **CL1**: $[Cu_3(\mathbf{L1})_3](PF_6)_3$, **CL2**: $[Cu_3(\mathbf{L2})_3](PF_6)_3$, or **CL7**: $[Cu_3(\mathbf{L7})_3](PF_6)_3$, respectively, as yellow plates, and the reaction of **L5** or **L6** with 1.7 equiv of $[Cu(CH_3CN)_4]BF_4$ in CH_2Cl_2 at room temperature gave the copper(I) complexes **CL5**: $[Cu_5(\mathbf{L5})_3](BF_4)_5$ or **CL6**: $[Cu_5(\mathbf{L5})_3](BF_4)_5$, respectively, as yellow powders. However, complexes (**CL5** and **CL6**) were each obtained as a diastereomer mixture, due to the difficulty of purifying the complex further.

Structure of Copper(I) Helicates. To investigate the structure of the copper(I) complexes obtained in this study, we tried to prepare single crystals of complexes. Recrystallization of **CL7** from CH_2Cl_2 by the slow diffusion of hexane vapor only gave small single crystals, which appeared to be suitable for X-ray structure analysis. The structural analysis showed **CL7** to be $[Cu_3(\mathbf{L7})_3](PF_6)_3$ (Fig. 4). Complex (**CL7**) belongs to space group $P2_1/c$, indicative of the racemic mixture of *P*- and *M*-helicates. Complex (**CL7**) consists of three copper(I) ions, three ligands, and three counterions. Selected bond distances and angles of **CL7** are shown in Table 2. Each Cu(I) ion has an approximately trigonal-planar geometry (the average N–Cu–N bond angles: 119.9°), which is similar to that reported by Potts et al.[4a] The Cu–N distances (1.980–2.045 Å) are unremarkable. No interaction between copper(I) ions is observed, because Cu1–Cu2 and Cu2–Cu3 bond distances are approximately 4.71 Å and 4.69 Å, respectively. No intrastrand π-stacking between pyridine rings is observed in **CL7**. Although X-ray quality crystals of copper(I) complexes other than **CL7** were not obtained, we determined on the basis of the crystal structure of **CL7** and the physicochemical data of the complexes, especially, the specific rotation (**CL1**, $[\alpha]_D$ -61.8 (c 0.98, CH_2Cl_2) for **CL1** and $[\alpha]_D$ $+60.7$ (c 1.32, CH_2Cl_2) for **CL2**), that the complexes (**CL1** and **CL2**) were chiral trinuclear triple-stranded helicates. Similarly, we determined that two pairs of complexes (**CL3** and **CL4**, **CL5** and **CL6**) were chiral tetra- and pentanuclear triple-stranded helicates, respectively, and that complex (**CL8**) was an achiral tetranuclear triple-stranded helicate. Figure 5 shows the schematic representations of the helical structures of tri-, tetra-, and pentanuclear triple-stranded helicates, respectively. These structures were also confirmed by elemental analysis and ESI-MS spectroscopy. The ESI-MS spectrum of trinuclear triple-stranded helicate (**CL1**), for example, has an average mass peak at m/z 1093.0 for $[\mathbf{CL1}\text{-}(PF_6)_2]^{2+}$; the ESI-MS spectrum of tetranuclear triple-stranded helicate (**CL4**) has average mass peaks at m/z 2671.0 for $[\mathbf{CL4}\text{-}(BF_4)]^+$ and 1292.0 for $[\mathbf{CL4}\text{-}(BF_4)_2]^{2+}$, and the ESI-MS spectrum of pentanuclear triple-stranded helicate (**CL5**) has an average mass peak at m/z 1519.0 for $[\mathbf{CL5}\text{-}(BF_4)_2]^{2+}$. Therefore, the stereoselective self-assembly of the copper(I) helicates has been achieved. The final determination as to whether the directionality within the each chiral copper(I) helicate is *P* or *M* is a next important subject, which will be

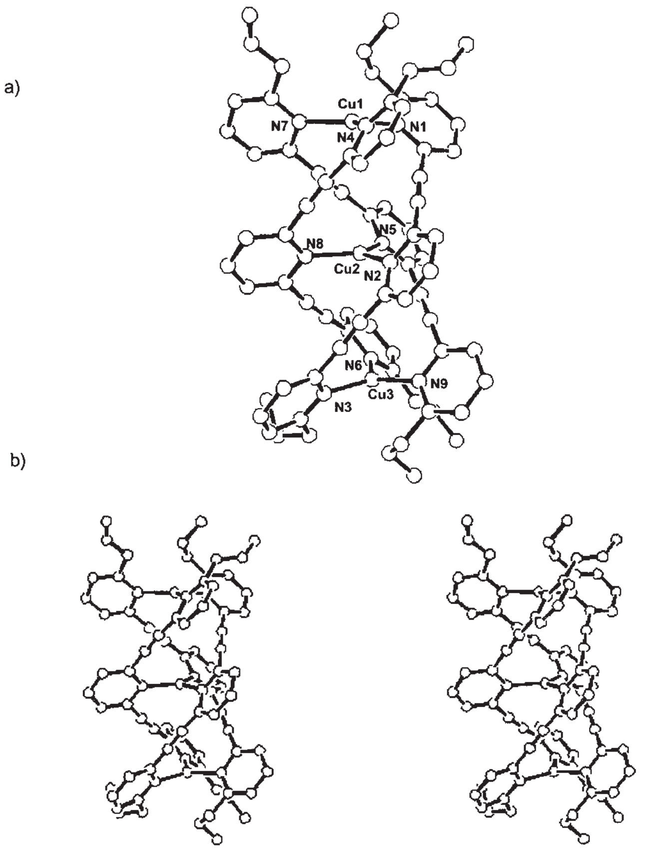


Fig. 4. (a) Ball-and-stick representation and (b) the stereotopic view of **CL7**. Solvate dichloromethane molecule and hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Bond Angles (°) of **CL7**

Cu1–N1, 2.036(5)	N1–Cu1–N4, 113.3(2)
Cu1–N4, 2.045(5)	N1–Cu1–N7, 124.6(2)
Cu1–N7, 2.013(5)	N4–Cu1–N7, 121.7(2)
Cu2–N2, 2.005(4)	N2–Cu2–N5, 112.2(2)
Cu2–N5, 1.993(4)	N2–Cu2–N8, 124.7(2)
Cu2–N8, 1.980(5)	N5–Cu2–N8, 123.1(2)
Cu3–N3, 2.022(4)	N3–Cu3–N6, 120.3(2)
Cu3–N6, 2.017(5)	N3–Cu3–N9, 116.9(2)
Cu3–N9, 2.018(4)	N6–Cu3–N9, 122.1(2)

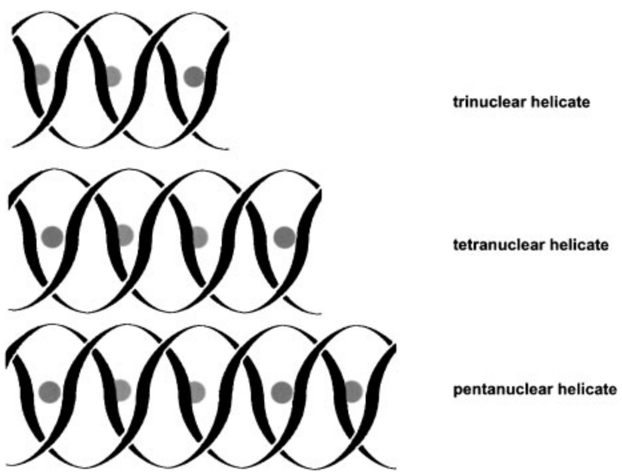


Fig. 5. Schematic representations of chiral tri-, tetra-, and pentanuclear triple-stranded helicates. Copper(I) ion and ligand molecule are marked with a circle and a thick line, respectively.

reported in detail elsewhere.

Behavior of Chiral Copper(I) Helicates in Solution. Complexes (**CL1–CL6**) are chiral complexes in the solid state. To observe the behavior of these chiral complexes in solution, we measured the specific rotation of chiral copper(I) complex (**CL3**), as a typical example, at 10-minute intervals (Fig. 6). The value of the specific rotation of **CL3** decreased exponentially, and the $[\alpha]_D$ value became approximately zero after about 24 hours. The inversion process could be observed by measurement of the ^{1}H NMR spectra of **CL3** at 8-hour intervals (Fig. 7). New signals were observed after 8 h and 48 h standing. The new signals are assigned to ^{1}H signals of a diastereomer of **CL3**, which has opposite helicity to **CL3**. These results suggest that an inversion[17] of helicity occurs in complex (**CL3**) by intramolecular mechanism. To investigate the inversion mechanism in further detail, we measured the ^{1}H NMR spectra of the 1:1 mixture of **CL3** and **CL8** (Fig. 8). As shown in Fig. 8, the ^{1}H NMR spectra became more complicated along with the appearance of new signals. This result indicates the generation of new copper(I) complexes with a variety of compositions such as a $[Cu_4(\mathbf{L3})_2(\mathbf{L8})]^{4+}$ framework. This framework was confirmed by ESI-MS spectroscopy, which showed the average mass peak at m/z 1268.0 for $\{[Cu_4(\mathbf{L3})_2(\mathbf{L8})](BF_4)_4\text{-}(BF_4)_2\}^{2+}$. Therefore, the conversion of a complex is also likely to be caused by the dissociation of the complex. Furthermore, copper(I) helicates in this study readily reverted to the parent ligands in quantitative yields by addition of a large excess amount of acetonitrile. This observation also suggests that the kinetic lability of the metal ions results in the dissociation of the complex in coordinating solvents.

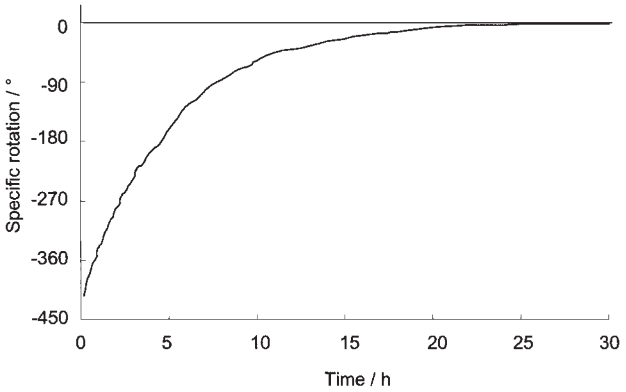


Fig. 6. Change in specific rotation of **CL3** in CH_2Cl_2.

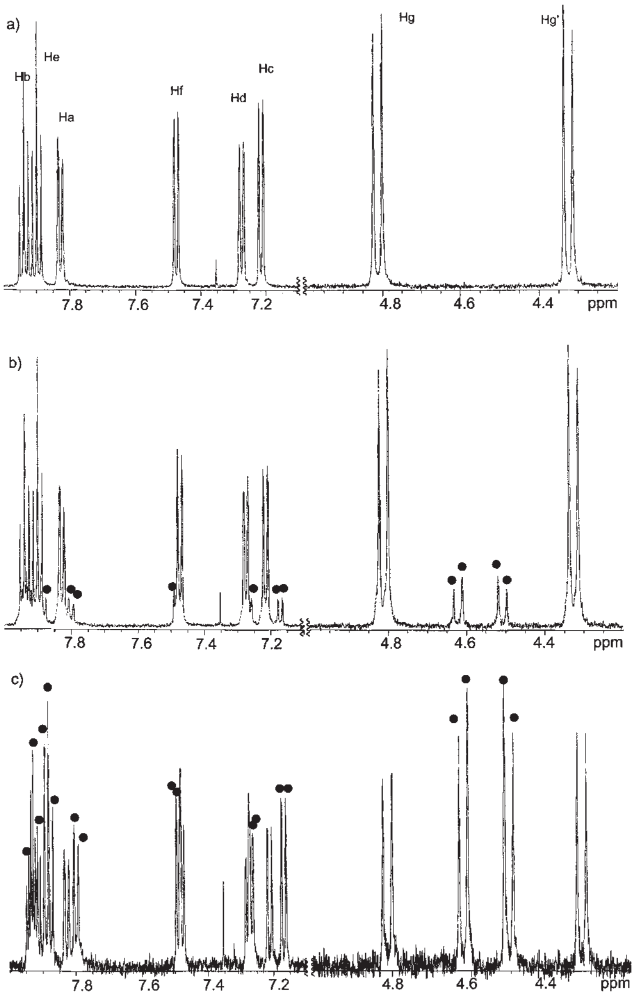


Fig. 7. Changes of the ^{1}H NMR spectra of **CL3**. a) 0 h; b) 8 h; c) 48 h. New signals are marked with a circle.

Conclusion

In conclusion, we have demonstrated that the coordination of chiral oligo(2-ethynylpyridines) with copper(I) ions proceeds smoothly to yield tri-, tetra-, and pentanuclear triple-stranded helicates in the solid state stereoselectively, and that the conversion of helicity of the copper(I) helicates takes place in solution. The chiral triple-stranded helicates described here would be applicable as an attractive catalyst for asymmetric

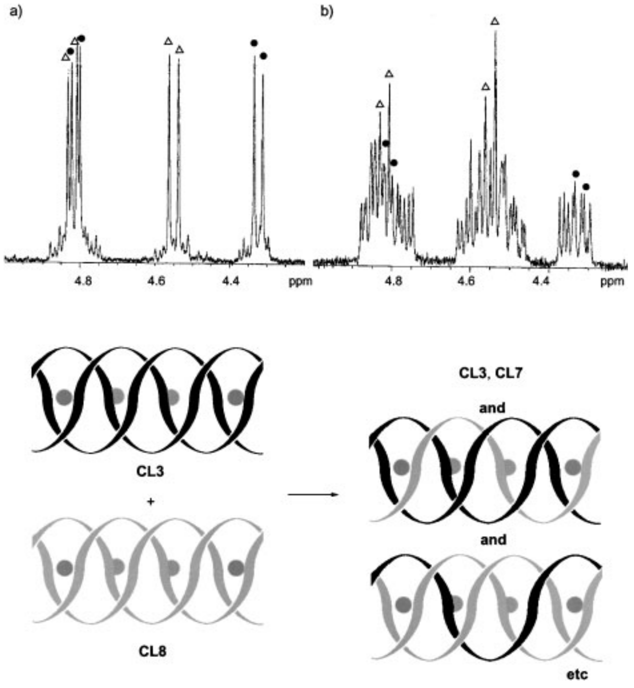


Fig. 8. Change of the ^{1}H NMR spectra of the 1:1 mixture of **CL3** and **CL7**. a) 0 h; b) 24 h. ^{1}H signals involved in **CL3** and **CL7**, which are assigned to the methylene protons substituted to the terminal pyridine ring, are marked with a circle and a triangle, respectively.

synthesis because they possess an asymmetric environment. Furthermore, a new (supra)molecular structure such as macrocyclic compounds or catenanes would be generated by using the copper(I) helicates as a synthetic template.

Experimental

General. All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions unless otherwise noted. Solvents and reagents were purified by literature methods where necessary.[18] All melting points were determined on a Yanagimoto micro melting point apparatus (Yanaco MP-500D) and are uncorrected. Infrared (IR) spectra were recorded on a Perkin-Elmer system 2000 FT-IR spectrometer. UV absorption spectra were obtained using a Hitachi 260-30 spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL JNM-LA400 (400 MHz) spectrometer; chemical shifts (δ) are reported in parts per million relative to tetramethylsilane (TMS). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; dsp, double of septets. Mass spectra (MS) were recorded on a JEOL JMS-600 mass spectrometer. Elemental analyses were performed by the Material Analysis Center of the Institute of Scientific and Industrial Research, Osaka University. Optical rotations were measured with a Perkin-Elmer 241 polarimeter. Circular dichroism spectroscopy was performed on a JASCO J-725 spectropolarimeter. Column chromatography was performed on Merck silica gel 60. 2-Bromo-6-(hydroxymethyl)pyridine (**3**), bromopyridine derivatives (**9a**, **9b**, **9e**, and **9f**), and 2,6-bis(ethynyl)pyridine were prepared from commercially available 2,6-dibromopyridine (**1a**) according to the literature procedure.

2-Bromo-6-(iodomethyl)pyridine 4. To a solution of 2-bromo-6-(hydroxymethyl)pyridine (**3**) (3.14 g, 16.7 mmol) in dry THF (70 mL) were added triethylamine (3.4 mL, 24.6 mmol) and 4-(dimethylamino)pyridine (0.102 g, 0.835 mmol) at room temperature. To the resulting solution was added dropwise methanesulfonyl chloride (2.0 mL, 25.8 mmol) at −40 °C. After being stirred at the same temperature for 2.5 h, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with AcOEt. The organic layer was washed successively with saturated aqueous $NaHCO_3$, H_2O, and brine, and then dried over anhydrous $MgSO_4$. After removal of the solvent, the oily residue was purified by column chromatography (silica gel, hexane–AcOEt) to give 2-bromo-6-(methylsulfonylmethyl)pyridine (4.23 g, 95%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (t, $J = 7.8$ Hz, 1H), 7.49 (d, $J = 7.6$ Hz, 1H), 7.45 (d, $J = 7.6$ Hz, 1H), 5.29 (s, 2H), 3.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 141.6, 139.4, 128.1, 121.0, 70.3, 38.1; IR (NaCl) 3000, 2910, 1570, 1545, 1425, 1395, 1345, 1160, 1110, 955, 820 cm^{-1}; FABMS (NBA) m/z 266 $[(M + H)^+]$; Found: C, 31.26; H, 2.92; N, 5.14; Br, 30.16; S, 11.91%. Calcd for $C_7H_8BrNO_3S$: C, 31.59; H, 3.03; N, 5.26; Br, 30.03; S, 12.05%.

To a solution of 2-bromo-6-(methylsulfonylmethyl)pyridine (3.93 g, 14.8 mmol) in acetone (150 mL) was added NaI (8.87 g, 59.18 mmol) at room temperature. After being heated under reflux for 5.5 h, the reaction mixture was cooled to room temperature, and then filtered through a pad of Celite. The solvent was evaporated to dryness under reduced pressure, and then the resulting oily residue was dissolved with AcOEt. The organic layer was washed successively with saturated aqueous $Na_2S_2O_3$, H_2O, and brine, and then dried over anhydrous $MgSO_4$. After removal of the solvent, the oily residue was purified by column chromatography (silica gel, hexane–AcOEt) to give **4** (4.31 g, 98%) as pale yellow crystals: mp 56.5–58.5 °C (dec); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (t, $J = 7.8$ Hz, 1H), 7.36 (d, $J = 7.6$ Hz, 1H), 7.35 (d, $J = 7.8$ Hz, 1H), 4.47 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 141.4, 139.2, 127.0, 121.9, 4.4; IR (NaCl) 3050, 1580, 1560, 1410, 1140, 880 cm^{-1}; FABMS (NBA) m/z 298 $[(M + H)^+]$; Found: C, 24.18; H, 1.59; N, 4.53; Br, 26.57; I, 42.79%. Calcd for C_6H_5BrIN: C, 24.19; H, 1.70; N, 4.70; Br, 26.82; I, 42.06%.

Diethyl (6-Bromo-2-pyridyl)methylphosphonate 5. The mixture of **4** (1.78 g, 5.97 mmol) and triethyl phosphite (2.0 mL) was stirred at 150 °C for 3 h. After being cooled to room temperature, the reaction mixture was evaporated to dryness under reduced pressure to give **5** (2.07 g, 99%) as an orange oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (t, $J = 7.7$ Hz, 1H), 7.38 (dd, $J = 8.1$, 2.6 Hz, 1H), 7.36 (dd, $J = 7.7$, 2.6 Hz, 1H), 4.15–4.07 (m, 4H), 3.39 (d, $J = 22$ Hz, 2H), 1.29 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.9, 153.9, 141.2, 141.2, 138.7, 138.7, 126.2, 126.1, 123.1, 123.0, 62.3, 62.3, 36.6, 35.3, 16.2, 16.1; FABMS (NBA) m/z 308 $[(M + H)^+]$; Found: C, 38.76; H, 5.12; Br, 25.88; N, 4.60; P, 10.19%. Calcd for $C_{10}H_{15}BrNO_3P$: C, 38.98; H, 4.91; Br, 25.93; N, 4.55; P, 10.05%.

1,2-Bis(6-bromo-2-pyridyl)ethene 6. To a suspension of NaH (60% dispersion in mineral oil, 0.350 g, 14.5 mmol) in dry THF (50 mL) was added a solution of **5** (4.50 g, 14.6 mmol) in dry THF (25 mL) at room temperature. After being heated under reflux for 1 h, the reaction mixture was cooled to room temperature, and then a solution of 2-bromo-6-formylpyridine (1.87 g, 10.0 mmol) in dry THF (25 mL) was added at the same temperature. The reaction mixture was stirred at room temperature for 20 h, and then quenched with saturated aqueous NH_4Cl and extracted with AcOEt. The organic layer was washed with H_2O and brine, and then dried over anhydrous $MgSO_4$. After removal of the solvent, the oily residue was purified by column chromatography (silica gel, benzene) to give **6** (3.14 g, 92%) as colorless needles: mp 197.0–198.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 2H), 7.54 (t, $J = 7.6$ Hz, 2H), 7.38 (d, $J = 7.8$ Hz, 2H), 7.35 (d, $J = 7.6$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 142.3, 138.9, 131.5, 127.1, 122.4; IR (neat) 3065, 1572, 1543, 1431, 1406, 1327, 1190, 1153, 1111, 974, 880, 791, 729 cm^{-1}; FABMS (NBA) m/z 341 $[(M + H)^+]$; Found: C, 42.40; H, 2.45; Br, 47.23; N, 8.19%. Calcd for $C_{12}H_8Br_2N_2$: C, 42.39; H, 2.37; Br, 47.00; N, 8.24%.

1,2-Bis(6-bromo-2-pyridyl)-1,2-dibromoethane 7. To a solution of **6** (1.84 g, 5.41 mmol) in chloroform (70 mL) was added dropwise a solution of bromine (0.42 mL, 8.15 mmol) in chloroform (30 mL) at room temperature. The reaction mixture was stirred at the same temperature for 2 h; then saturated aqueous $Na_2S_2O_3$ was added. The resulting precipitate was collected and washed with H_2O and chloroform to give **7** (2.48 g, 92%) as a white powder: mp 249.0 °C (dec.); ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.88 (t, $J = 7.3$ Hz, 2H), 7.85 (d, $J = 7.3$ Hz, 2H), 7.68 (d, $J = 7.3$ Hz, 2H), 6.06 (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 158.7, 141.3, 141.0, 128.7, 123.3, 51.7; IR (neat) 3085, 2999, 1578, 1549, 1427, 1406, 1180, 1153, 1116, 988, 870, 799, 737 cm^{-1}; Found: C, 28.81; H, 1.57; Br, 64.23; N, 5.59%. Calcd for $C_{12}H_8Br_4N_2$: C, 28.84; H, 1.61; Br, 63.95; N, 5.60%.

1,2-Bis(6-bromo-2-pyridyl)ethyne 1b. To a solution of potassium *t*-butoxide (0.140 g, 1.25 mmol) in dry CH_2Cl_2 (20 mL) was added **7** (0.300 g, 0.600 mmol) at −20 °C. After being stirred at room temperature for 24 h, the reaction mixture was quenched with saturated aqueous NH_4Cl and then extracted with CH_2Cl_2. The organic layer was washed with H_2O and brine, and then dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was recrystallized from CH_2Cl_2–hexane to give **1b** (0.180 g, 90%) as a white powder: mp 212.0–214.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, $J = 3.8$ Hz, 2H), 7.58 (d, $J = 5.4$ Hz, 2H), 7.51 (dd, $J = 5.2$, 3.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.6, 142.0, 138.5, 128.4, 126.7, 87.8; IR (KBr) 3045, 2356, 1573, 1545, 1442, 1123, 790 cm^{-1}; FABMS (NBA) m/z 339 $[(\mathrm{M}+\mathrm{H})^+]$; Found: C, 42.65; H, 1.82; Br, 47.03; N, 8.09%. Calcd for $C_{12}H_6Br_2N_2$: C, 42.64; H, 1.79; Br, 47.28; N, 8.29%.

2-Ethynyl-6-(trimethylsilylethynyl)pyridine 8. To a solution of 2,6-bis(ethynyl)pyridine (5.60 g, 44.0 mmol) was added dropwise ethylmagnesium bromide, which was prepared from ethyl bromide (3.6 mL, 48.3 mmol), Mg turnings (1.18 g, 48.6 mmol) and dry THF (100 mL), at room temperature. After being stirred at the same temperature for 2.5 h, the reaction mixture was quenched with saturated aqueous NH_4Cl, and extracted with AcOEt. The organic layer was washed with H_2O and brine, and then dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography (silica gel, hexane–AcOEt) to give **8** (5.61 g, 64%) as a yellow powder: mp 78.8–79.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (t, $J = 7.8$ Hz, 1H), 7.43 (d, $J = 7.8$ Hz, 1H), 7.41 (d, $J = 7.8$ Hz, 1H), 3.14 (s, 1H), 0.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 142.5, 136.4, 126.6, 102.9, 95.6, 82.2, 77.6, -0.4; FABMS (NBA) m/z 200 $[(\mathrm{M}+\mathrm{H})^+]$; Found: C, 72.39; H, 6.60; N, 6.99%. Calcd for $C_{12}H_{13}NSi$: C, 72.31; H, 6.57; N, 7.03%.

2-[(L)-Menthyloxymethyl]-6-(trimethylsilylethynyl)pyridine 10a. To a solution of 6-bromo-2-[(L)-menthyloxymethyl]pyridine (**9a**) (1.60 g, 4.90 mmol) in dry diethylamine (50 mL) was added tetrakis(triphenylphosphine)palladium(0) (0.265 g, 0.229 mmol) at room temperature. To the resulting solution was added dropwise trimethylsilylacetylene (1.6 mL, 11.3 mmol) at the same temperature. After being stirred at the same temperature for 18 h, the reaction mixture was cooled to room temperature and then filtered through a pad of Celite. The filtrate was evaporated to dryness under reduced pressure to give an oily residue. The residue was purified by column chromatography (silica gel, hexane–AcOEt) to give **10a** (1.67 g, 99%) as a yellow oil: $[\alpha]_D$ -63.5 (c 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (t, $J = 7.8$ Hz, 1H), 7.46 (d, $J = 7.8$ Hz, 1H), 7.35 (d, $J = 7.6$ Hz, 1H), 4.78(d, $J = 13.7$ Hz, 1H), 4.54 (d, $J = 13.7$ Hz, 1H), 3.22 (dt, $J = 10.5$, 4.1 Hz, 1H), 2.28 (dsp, $J = 6.8$, 2.7 Hz, 1H), 2.18–2.14 (m, 1H), 1.68–1.61 (m, 2H), 1.43–1.19 (m, 2H), 1.04–0.78 (m, 9H), 0.74 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 141.7, 136.4, 125.8, 120.6, 103.6, 94.3, 79.5, 71.0, 48.2, 40.2, 34.4, 31.4, 25.6, 23.1, 22.2, 20.9, 16.1, -0.4; IR (neat): 2954, 2920, 2868, 1582, 1568, 1447, 1250, 1113, 932, 843, 797, 760 cm^{-1}; FABMS (NBA) m/z 344 $[(\mathrm{M}+\mathrm{H})^+]$; Found: C, 73.69; H, 9.52; N, 4.20%. Calcd for $C_{21}H_{33}NOSi$: C, 73.41; H, 9.68; N, 4.08%.

2-[(D)-Menthyloxymethyl]-6-(trimethylsilylethynyl)pyridine 10b. This compound was prepared from 6-bromo-2-[(D)-menthyloxymethyl]pyridine (**9b**) and trimethylsilylacetylene according to the method used for the preparation of **10a**. Yellow oil; yield 90%; $[\alpha]_D$ $+64.0$ (c 1.3, $CHCl_3$).

2-[6-(L)-Menthyloxymethyl-2-pyridylethynyl]-6-(trimethylsilylethynyl)pyridine 10c. This compound was prepared from 6-bromo-2-[(L)-menthyloxymethyl]pyridine (**9a**) and compound (**8**) according to the method used for the preparation of **10a**. Yellow powder; yield 83%; mp 99.8–100.8 °C; $[\alpha]_D$ -54.2 (c 1.07, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (t, $J = 7.8$ Hz, 1H), 7.57 (t, $J = 7.8$ Hz, 1H), 7.45 (d, $J = 6.8$ Hz, 1H), 7.44 (d, $J = 6.8$ Hz, 1H), 7.36 (d, $J = 7.8$ Hz, 2H), 4.74 (d, $J = 13.7$ Hz, 1H), 4.50 (d, $J = 13.7$ Hz, 1H), 3.18 (dt, $J = 10.7$, 4.4 Hz, 1H), 2.23 (dsp, $J = 7.0$, 2.9 Hz, 1H), 2.22–2.17 (m, 1H), 1.62–1.55 (m, 2H), 1.36–1.23 (m, 2H), 0.98–0.78 (m, 9H), 0.67 (d, $J = 6.8$ Hz, 3H), 0.21 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 143.4, 142.9, 141.1, 136.7, 136.3, 126.9, 126.8, 126.2, 121.3, 102.9, 95.5, 88.1, 87.1, 79.5, 71.0, 48.2, 40.2, 34.4, 31.4, 25.6, 23.1, 22.2, 20.9, 16.0, -0.42; IR (KBr) 2940, 2850, 1580, 1450, 1250, 1115, 840 cm^{-1}; FABMS (NBA) m/z 445 $[(\mathrm{M}+\mathrm{H})^+]$; Found: C, 75.76; H, 8.10; N, 6.26%. Calcd for $C_{28}H_{36}N_2OSi$: C, 75.61; H, 8.18; N, 6.30%.

2-[6-(D)-Menthyloxymethyl-2-pyridylethynyl]-6-(trimethylsilylethynyl)pyridine 10d. This compound was prepared from 6-bromo-2-[(D)-menthyloxymethyl]pyridine (**9b**) and compound (**8**) according to the method used for the preparation of **10a**. Yellow powder; yield 85%; $[\alpha]_D$ $+50.2$ (c 1.20, $CHCl_3$).

2-(Methyloxymethyl)-6-(trimethylsilylethynyl)pyridine 10e. This compound was prepared from 6-bromo-2-(methoxymethyl)pyridine (**9e**) and trimethylsilylacetylene according to the method used for the preparation of **10a**. Colorless oil; yield 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (t, $J = 7.8$ Hz, 1H), 7.37 (d, $J = 8.8$ Hz, 1H), 7.35 (d, $J = 8.3$ Hz, 1H), 4.55 (s, 2H), 3.43 (s, 3H), 0.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 142.2, 136.6, 126.1, 120.4, 103.6, 94.7, 75.2, 58.7, -0.3; IR (neat) 2950, 2900, 2850, 2150, 1580, 1440, 1250, 1120, 920, 840, 760 cm^{-1}; FABMS (NBA) m/z 220 $[(\mathrm{M}+\mathrm{H})^+]$; Found: C, 65.53; H, 7.80; N, 6.13%. Calcd for $C_{12}H_{17}NOSi$: C, 65.71; H, 7.81; N, 6.39%.

2-[(*t*-Butyldimethylsilyloxy)methyl]-6-(trimethylsilylethynyl)pyridine 10f. This compound was prepared from 2-bromo-6-[(*t*-butyldimethylsilyloxy)methyl]pyridine (**9f**) and trimethylsilylacetylene according to the method used for the preparation of **10a**. Yellow oil; yield 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (t, $J = 7.8$ Hz, 1H), 7.47 (dd, $J = 7.8$, 0.7 Hz, 1H), 7.33 (dd, $J = 7.6$, 0.5 Hz, 1H), 4.83 (s, 2H), 0.95 (s, 9H), 0.26 (s, 9H), 0.12 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 141.8, 136.6, 125.5, 119.3, 103.7, 94.4, 65.9, 25.9, 18.3, -0.3, -5.5; IR (neat) 3048, 2958, 2857, 2165, 1558, 1454, 1252, 1121, 843 cm^{-1} FABMS (NBA) m/z 320 $[(\mathrm{M}+\mathrm{H})^+]$; Found: C, 64.00; H, 8.83; N, 4.23%. Calcd for $C_{17}H_{29}NOSi_2$: C, 63.89; H, 9.15; N, 4.38%.

2-Ethynyl-6-[(L)-menthyloxymethyl]pyridine 2a. To a solution of **10a** (2.60 g, 7.57 mmol) in methanol (60 mL) was added potassium carbonate (0.052 g, 0.376 mmol) at 0 °C. After being stirred at the same temperature for 8 h, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with AcOEt. The organic layer was washed with H_2O and brine, and then dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography (silica gel, hexane–AcOEt) to give **2a** (1.86 g, 90%) as a yellow oil: $[\alpha]_D$ -83.5 (c 2.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (t, $J = 7.6$ Hz, 1H), 7.51 (d, $J = 7.8$ Hz, 1H), 7.37 (d, $J = 7.6$ Hz, 1H), 4.78 (d, $J = 13.7$ Hz, 1H), 4.54 (d, $J = 13.9$ Hz, 1H), 3.23 (dt, $J = 10.5$, 4.1 Hz, 1H), 3.14 (s, 1H), 2.29 (dsp, $J = 6.8$, 2.7 Hz, 1H), 2.19–2.15 (m, 1H), 1.69–1.62 (m, 2H), 1.39–1.21 (m, 2H), 1.04–0.78 (m, 9H), 0.73 (d, $J = 6.8$ Hz, 3H); FABMS (NBA) m/z 272 $[(\mathrm{M}+\mathrm{H})^+]$. This compound and the other ethynylpyridine derivatives (**2b–f**) were immediately used for the next steps without further purification, because compounds (**2a–f**) decomposed easily. Compounds (**2b–f**) were prepared according to the method used for the preparation of **2a**.

2-Ethynyl-6-[(D)-menthyloxymethyl]pyridine 2b. Yellow oil; yield 86%; $[\alpha]_D$ $+84.8$ (c 2.7, $CHCl_3$).

2-Ethynyl-6-[6-(L)-menthyloxymethyl-2-pyridylethynyl]pyridine 2c. Yellow powder; yield 95%; mp 112.4–113.2 °C; $[\alpha]_D$ -60.7 (c 1.22, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (t, $J = 7.8$ Hz, 1H), 7.65 (t, $J = 7.8$ Hz, 1H), 7.56 (d, $J = 7.8$ Hz, 1H), 7.49 (d, $J = 7.8$ Hz, 1H), 7.47 (d, $J = 7.8$ Hz, 1H), 7.42 (d, $J = 7.6$ Hz, 1H), 4.77 (d, $J = 13.7$ Hz, 1H), 4.53 (d, $J = 13.7$ Hz, 1H), 3.21 (dt, $J = 10.7$, 4.4 Hz, 1H), 3.15 (s, 1H), 2.26 (dsp, $J = 7.0$, 2.9 Hz, 1H), 2.16–2.10 (m, 1H), 1.65–1.59 (m, 2H), 1.39–1.26 (m, 2H), 1.01–0.78 (m, 9H), 0.70 (d, $J = 6.8$ Hz, 3H); FABMS (NBA) m/z 373 $[(\mathrm{M}+\mathrm{H})^+]$.

2-Ethynyl-6-[6-(D)-menthyloxymethyl-2-pyridylethynyl]-

pyridine 2d. Yellow powder; yield 93%; $[\alpha]_D$ +60.0 (*c* 1.50, $CHCl_3$).

2-Ethynyl-6-(methoxymethyl)pyridine 2e. Pale yellow oil; yield 88%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (t, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 4.58 (s, 2H), 3.47 (s, 3H), 3.17 (s, 1H); FABMS (NBA) *m/z* 148 $[(M+H)^+]$.

2-(*t*-Butyldimethylsilyloxymethyl)-6-(ethynyl)pyridine 2f. Orange oil; yield 97%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (t, *J* = 7.8 Hz, 1H), 7.52 (dd, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 4.83 (s, 2H), 3.13 (s, 1H), 0.96 (s, 9H), 0.12 (s, 6H); FABMS (NBA) *m/z* 248 $[(M+H)^+]$.

2,6-Bis{6-[(L)-menthyloxymethyl]-2-pyridylethynyl}pyridine L1. To a solution of 2,6-dibromopyridine (**1a**) (0.240 g, 1.01 mmol) in diethylamine (40 mL) were added a solution of **2a** (0.631 g, 2.32 mmol) in triethylamine (20 mL) and tetrakis(triphenylphosphine)palladium(0) (0.060 g, 0.052 mmol) at room temperature. After being stirred at 90 °C for 18 h, the reaction mixture was cooled to room temperature, and then filtered through a pad of Celite. The filtrate was evaporated to dryness under reduced pressure to give an oily residue. The residue was purified by column chromatography (silica gel, AcOEt) to give **L1** (0.574 g, 92%) as colorless plates: mp 121.5–122.5 °C; $[\alpha]_D$ −74.6 (*c* 1.08, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.74 (m, 3H), 7.58 (d, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 4H), 4.78 (d, *J* = 13.4 Hz, 2H), 4.52 (d, *J* = 13.7 Hz, 2H), 3.25 (dd, *J* = 4.2, 6.3 Hz, 2H), 2.30 (m, 2H), 2.19 (m, 2H), 1.69–1.62 (m, 4H), 1.46–1.29 (m, 4H), 1.10–0.83 (m, 18H), 0.77 (d, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 161.1, 143.5, 141.5, 137.3, 137.1, 127.5, 126.6, 121.8, 88.6, 87.1, 80.0, 71.4, 48.8, 40.7, 35.0, 31.9, 26.2, 23.7, 22.5, 21.2, 16.4; IR (KBr) 2900, 2850, 2210, 1555, 1430, 1090, 770 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ε) 320 (4.6), 294 (4.5), 265 (4.4) nm; FABMS (NBA) *m/z* 618 $[(M+H)^+]$; Found: C, 79.64; H, 8.08; N, 6.93%. Calcd for $C_{41}H_{51}N_3O_2$: C, 79.69; H, 8.34; N, 6.80%.

2,6-Bis{6-[(D)-menthyloxymethyl]-2-pyridylethynyl}pyridine L2. This compound was prepared from **1a** and **2b** according to the method used for the preparation of **L1**. Colorless plates; yield 90%; $[\alpha]_D$ +73.5 (*c* 0.98, $CHCl_3$); Found: C, 79.87; H, 8.13; N, 6.59%. Calcd for $C_{41}H_{51}N_3O_2$: C, 79.69; H, 8.34; N, 6.80%.

1,2-Bis(6-{6-[(L)-menthyloxymethyl]-2-pyridylethynyl}-2-pyridyl)acetylene L3. This compound was prepared from **1b** and **2a** according to the method used for the preparation of **L1**. White powder; yield: 86%; mp 201.0–203.0 °C; $[\alpha]_D$ −60.2 (*c* 1.08, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (t, *J* = 7.7 Hz, 2H), 7.72 (t, *J* = 7.7 Hz, 2H), 7.62 (dd, *J* = 7.7, 1.1 Hz, 2H), 7.62 (dd, *J* = 7.7, 1.1 Hz, 2H), 7.54 (d, *J* = 7.7 Hz, 4H), 4.82 (d, *J* = 13.6 Hz, 2H), 4.58 (d, *J* = 13.6 Hz, 2H), 3.25 (dt, *J* = 10.6, 4.4 Hz, 2H), 2.30 (dsp, *J* = 7.0, 2.6 Hz, 2H), 2.22–2.17 (m, 2H), 1.68–1.59 (m, 4H), 1.39–1.32 (m, 4H), 1.01–0.86 (m, 18H), 0.75 (d, *J* = 7.0 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.6, 143.3, 143.0, 141.2, 136.8, 136.7, 127.5, 127.4, 126.4, 121.5, 88.5, 87.8, 87.0, 79.7, 71.1, 48.3, 40.4, 34.5, 31.5, 25.7, 23.3, 22.3, 21.0, 16.2; IR (neat) 2964, 2918, 2847, 1582, 1556, 1454, 1107, 984, 797, 729 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ε) 322 (4.5), 296 (4.4), 266 (4.3) nm; FABMS (NBA) *m/z* 719 $[(M+H)^+]$; Found: C, 79.95; H, 7.24; N, 7.55%. Calcd for $C_{48}H_{54}N_4O_2$: C, 80.19; H, 7.57; N, 7.79%.

1,2-Bis(6-{6-[(D)-menthyloxymethyl]-2-pyridylethynyl}-2-pyridyl)acetylene L4. This compound was prepared from **1b** and **2b** according to the method used for the preparation of **L1**. White powder; yield: 86%; $[\alpha]_D$ +60.1 (*c* 1.15, $CHCl_3$); Found: C, 79.90; H, 7.40; N, 7.63%. Calcd for $C_{48}H_{54}N_4O_2$: C, 80.19; H, 7.57; N, 7.79%.

2,6-Bis(6-{6-[(L)-menthyloxymethyl]-2-pyridylethynyl}-2-pyridylethynyl)pyridine L5. This compound was prepared from **1a** and **2c** according to the method used for the preparation of **L1**. White powder; yield: 75%; mp 230 °C (dec.); $[\alpha]_D$ −54.6 (*c* 1.12, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (t, *J* = 7.7 Hz, 1H), 7.74 (t, *J* = 7.7 Hz, 2H), 7.73 (t, *J* = 7.7 Hz, 2H), 7.64 (d, *J* = 7.7 Hz, 2H), 7.63 (dd, *J* = 7.7, 1.1 Hz, 2H), 7.62 (dd, *J* = 7.7, 1.1 Hz, 2H), 7.54 (d, *J* = 7.7 Hz, 4H), 4.82 (d, *J* = 13.6 Hz, 2H), 4.58 (d, *J* = 13.6 Hz, 2H), 3.25 (dt, *J* = 10.7, 4.4 Hz, 2H), 2.31 (dsp, *J* = 7.0, 2.9 Hz, 2H), 2.22–2.17 (m, 2H), 1.68–1.59 (m, 4H), 1.40–1.31 (m, 4H), 1.03–0.84 (m, 18H), 0.75 (d, *J* = 7.0 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.6, 143.3, 143.0, 142.9, 141.2, 136.8, 136.8, 136.7, 127.6, 127.5, 127.4, 126.5, 121.5, 88.5, 87.8, 87.7, 87.0, 79.7, 71.1, 48.3, 40.4, 34.5, 31.5, 25.7, 23.2, 22.3, 21.0, 16.2; IR (neat) 2955, 2918, 2866, 1582, 1556, 1454, 1335, 1285, 1161, 1109, 984, 797, 727 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ε) 324 (4.6), 296 (4.5), 267 (4.4) nm; FABMS (NBA) *m/z* 820 $[(M+H)^+]$; Found: C, 80.34; H, 6.87; N, 8.41%. Calcd for $C_{55}H_{57}N_5O_2$: C, 80.55; H, 7.01; N, 8.54%.

2,6-Bis(6-{6-[(D)-menthyloxymethyl]-2-pyridylethynyl}-2-pyridylethynyl)pyridine L6. This compound was prepared from **1a** and **2d** according to the method used for the preparation of **L1**. White powder; yield: 72%; $[\alpha]_D$ +53.6 (*c* 1.05, $CHCl_3$); Found: C, 80.44; H, 6.98; N, 8.26%. Calcd for $C_{55}H_{57}N_5O_2$: C, 80.55; H, 7.01; N, 8.54%.

2,6-Bis[(6-methoxymethyl)-2-pyridylethynyl]pyridine L7. This compound was prepared from **1a** and **2e** according to the method used for the preparation of **L1**. Colorless plates; yield 93%; mp 111.5–113.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (t, *J* = 7.8 Hz, 2H), 7.71 (dd, *J* = 8.5, 8.7 Hz, 1H), 7.61 (dd, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.46 (d, *J* = 7.8 Hz, 2H), 4.62 (s, 4H), 3.49 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 143.1, 141.6, 136.8, 136.5, 127.2, 126.2, 121.0, 88.3, 87.2, 75.2, 58.8; IR (KBr) 2960, 2920, 2800, 2200, 1580, 1450, 1100, 980, 910, 800, 790 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ε) 319 (4.6), 293 (4.5), 264 (4.4) nm; FABMS (NBA) *m/z* 370 $[(M+H)^+]$; Found: C, 74.64; H, 5.09; N, 11.39%. Calcd for $C_{23}H_{19}N_3O_2$: C, 74.78; H, 5.18; N, 11.37%.

1,2-Bis(6-{6-[*t*-butyldimethylsilyloxymethyl]-2-pyridylethynyl}-2-pyridyl)acetylene L8. This compound was prepared from **1b** and **2f** according to the method used for the preparation of **L1**. White powder; yield: 96%; mp 216 °C (dec.); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (t, *J* = 7.7 Hz, 2H), 7.73 (t, *J* = 7.3 Hz, 2H), 7.62 (d, *J* = 7.7 Hz, 4H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 7.7 Hz, 2H), 4.87 (s, 4H), 0.97 (s, 18H), 0.13 (s, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.2, 143.2, 142.9, 141.1, 136.9, 136.6, 127.4, 127.4, 126.1, 120.0, 88.5, 87.7, 86.9, 65.8, 25.9, 18.3, −5.4; IR (KBr) 3054, 2930, 2857, 2327, 1577, 1461, 1254, 1112, 852 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ε) 323 (4.65), 302 (4.49), 294 (4.53), 275 (4.47), 262 (4.53) nm; FABMS (NBA) *m/z* 671 $[(M+H)^+]$; Found: C, 71.46; H, 6.72; N, 8.15%. Calcd for $C_{40}H_{46}N_4O_2Si_2$: C, 71.60; H, 6.91; N, 8.35%.

Chiral Trinuclear Copper(I) Helicate CL1: $[Cu_3(L1)_3](PF_6)_3$. To a solution of tetrakis(acetonitrile)copper(I) hexafluorophosphate (1.14 g, 2.98 mmol) in dichloromethane (30 mL) was added dropwise a solution of **L1** (1.84 g, 2.98 mmol) in dichloromethane (70 mL) at room temperature. After being stirred at the same temperature for 12 h, the reaction solution was evaporated to dryness under reduced pressure to give the crude yellow crystals. Recrystallization of the crude crystals from dichloromethane–hexane gave the pure complex (**CL1**) (2.38 g, 97%) as yellow crystals: mp 238–239 °C; $[\alpha]_D$ −61.8 (*c* 0.92, CH_2Cl_2); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.93 (t, *J* = 7.8, 8.1 Hz, 2H), 7.87–7.79 (m, 3H), 7.28–7.17 (m, 4H), 4.82 (d, *J* = 13.4 Hz, 1H), 4.62 (d, *J* = 13.2 Hz, 1H), 4.52 (d, *J* = 13.2 Hz, 1H), 4.33 (d, *J* = 13.7 Hz, 1H), 3.20–3.08 (m, 2H), 2.14 (t, *J* = 7.1, 6.8 Hz, 2H), 1.62 (ddd, *J* = 11.7, 10.2 Hz, 6H), 1.28–1.16 (m, 4H), 0.99–0.70 (m, 18H), 0.66 (d, $J = 7.1$ Hz, 3H), 0.52 (q, $J = 11.5$, 11.7 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 159.6, 159.2, 140.1, 139.6, 139.1, 128.6, 128.1, 124.9, 88.8, 80.7, 70.2, 69.8, 47.7, 47.5, 39.9, 39.5, 33.8, 31.1, 25.7, 25.4, 22.9, 22.7, 21.8, 21.6, 20.4, 15.9, 15.4; IR (KBr) 2875, 2820, 1570, 1540, 1440, 1095, 1065, 820, 783 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ε) 297 (4.49), 227 (4.56) nm; Found: C, 59.33; H, 6.08; N, 5.06; P, 3.90; F, 13.89%. Calcd for $C_{41}H_{51}CuF_6N_3O_2P$: C, 59.58; H, 6.23; N, 5.09; P, 3.75; F, 13.79%.

Chiral Trinuclear Copper(I) Helicate CL2: $[Cu_3(L2)_3](PF_6)_3$. This compound was prepared from **L2** and $[Cu(CH_3CN)_4]PF_6$ in 1:1 ratio according to the methods used for the preparation of **CL1**. Yellow crystals; yield 95%; $[\alpha]_D$ +60.7 (c 1.32, CH_2Cl_2); Found: C, 59.36; H, 6.08; N, 5.36; P, 3.48; F, 13.84%. Calcd for $C_{41}H_{51}CuF_6N_3O_2P$: C, 59.58; H, 6.23; N, 5.09; P, 3.75; F, 13.79%.

Chiral Tetranuclear Copper(I) Helicate CL3: $[Cu_4(L3)_3](BF_4)_4$. This compound was prepared from **L3** and $[Cu(CH_3CN)_4]BF_4$ in 1:1.4 ratio according to the methods used for the preparation of **CL1**. Yellow blocks; yield 92%; mp 264 °C (dec.); $[\alpha]_D$ −418 (c 0.96, CH_2Cl_2); ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.94 (t, $J = 7.7$ Hz, 6H), 7.90 (t, $J = 7.7$ Hz, 6H), 7.83 (d, $J = 7.3$ Hz, 6H), 7.47 (dd, $J = 7.7$, 1.1 Hz, 6H), 7.28 (dd, $J = 7.7$, 0.7 Hz, 6H), 7.21 (dd, $J = 8.1$, 1.1 Hz, 6H), 4.81 (d, $J = 13.6$ Hz, 6H), 4.33 (d, $J = 13.6$ Hz, 6H), 3.10 (dt, $J = 10.6$, 4.4 Hz, 6H), 2.12 (dsp, $J = 7.3$, 2.9 Hz, 6H), 1.72–1.69 (m, 6H), 1.66–1.61 (m, 12H), 1.26–1.21 (m, 12H), 0.94–0.75 (m, 54H), 0.65 (d, $J = 7.0$ Hz, 18H); IR (neat) 3084, 2950, 2920, 2868, 2361, 1587, 1555, 1466, 1049, 804 cm^{-1}; Found: C, 62.49; H, 5.71; F, 11.15; N, 6.14%. Calcd for $C_{144}H_{162}B_4Cu_4F_{16}N_{12}O_6$: C, 62.70; H, 5.92; F, 11.02; N, 6.09%.

Chiral Tetranuclear Copper(I) Helicate CL4: $[Cu_4(L4)_3](BF_4)_4$. This compound was prepared from **L4** and $[Cu(CH_3CN)_4]BF_4$ in 1:1.4 ratio according to the methods used for the preparation of **CL1**. Yellow blocks; yield: 95%; $[\alpha]_D$ +422 (c 1.12, CH_2Cl_2).

Chiral Pentanuclear Copper(I) Helicate CL5: $[Cu_5(L5)_3](BF_4)_5$. This compound was prepared as a diastereomer mixture from **L5** and $[Cu(CH_3CN)_4]BF_4$ in 1:1.7 ratio according to the methods used for the preparation of **CL1**. Yellow powder; yield 89%; ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.96–7.87 (m, 6H), 7.83 (d, $J = 7.7$ Hz, 2H), 7.81 (d, $J = 8.1$ Hz, 1/3H), 7.49 (dd, $J = 8.1$, 1.1 Hz, 1/3H), 7.47 (dd, $J = 8.1$, 1.1 Hz, 2H), 7.46 (d, $J = 8.1$ Hz, 2H), 7.44 (d, $J = 8.4$ Hz, 1/3H), 7.27 (d, $J = 7.7$ Hz, 2H), 7.26 (d, $J = 8.4$ Hz, 1/3H), 7.23 (dd, $J = 7.7$, 1.1 Hz, 6H), 7.18 (dd, $J = 8.1$, 0.7 Hz, 1/3H), 4.81 (d, $J = 13.9$ Hz, 2H), 4.63 (d, $J = 12.8$ Hz, 1/3H), 4.51 (d, $J = 12.8$ Hz, 1/3H), 4.33 (d, $J = 13.6$ Hz, 2H), 3.17 (dt, $J = 10.6$, 4.4 Hz, 1/3H), 3.10 (dt, $J = 10.6$, 4.1 Hz, 2H), 2.15–2.09 (m, 7/3H), 1.72–1.70 (m, 7/3H), 1.66–1.61 (m, 7/3H), 1.26–1.21 (m, 5H), 0.95–0.77 (m, 22H), 0.65 (d, $J = 7.0$ Hz, 6H); Found: C, 61.68; H, 5.31; F, 11.96; N, 6.66%. Calcd for $C_{165}H_{171}B_5Cu_5F_{20}N_{15}O_6$: C, 61.70; H, 5.37; F, 11.83; N, 6.54%.

Chiral Pentanuclear Copper(I) Helicate CL6: $[Cu_5(L6)_3](BF_4)_5$. This compound was prepared as a diastereomer mixture from **L6** and $[Cu(CH_3CN)_4]BF_4$ in 1:1.7 ratio according to the methods used for the preparation of **CL1**. Yellow powder; yield 91%; Found: C, 61.77; H, 5.36; F, 11.90; N, 6.72%. Calcd for $C_{165}H_{171}B_5Cu_5F_{20}N_{15}O_6$: C, 61.70; H, 5.37; F, 11.83; N, 6.54%.

Achiral Trinuclear Copper(I) Helicate CL7: $[Cu_3(L7)_3](PF_6)_3$. This compound was prepared from **L7** and $[Cu(CH_3CN)_4]PF_6$ in 1:1 ratio according to the methods used for the preparation of **CL1**. Yellow prisms; yield 96%; mp >300 °C; ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.86 (t, $J = 7.8$ Hz, 6H), 7.79 (t, $J = 7.8$ Hz, 3H), 7.68 (d, $J = 7.8$ Hz, 6H), 7.15 (d, $J = 8.1$ Hz, 6H), 7.14 (d, $J = 8.1$ Hz, 6H), 4.58 (d, $J = 13.4$ Hz, 6H), 4.38 (d, $J = 13.4$ Hz, 6H), 3.30 (s, 18H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 158.9, 140.8, 140.4, 139.9, 139.8, 129.0, 128.8, 125.6, 89.7, 89.2, 74.7, 59.2; IR (KBr) 3030, 2890, 2780, 1570, 1540, 1440, 1100, 820, 785 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ε) 295 (4.42), 232 (4.42) nm; Found: C, 47.52; H, 3.11; N, 7.25; P, 5.20; F, 19.55%. Calcd for $C_{69}H_{57}Cu_3F_{18}N_9O_6P_3$: C, 47.80; H, 3.31; N, 7.27; P, 5.36; F, 19.72%.

Achiral Tetranuclear Copper(I) Helicate CL8: $[Cu_4(L8)_3](BF_4)_4$. This compound was prepared from **L7** and $[Cu(CH_3CN)_4]BF_4$ in 1:1.4 ratio according to the methods used for the preparation of **CL1**. Yellow blocks; yield 96%; mp 256 °C (dec.); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.96 (t, $J = 7.8$ Hz, 6H), 7.85 (t, $J = 7.8$ Hz, 12H), 7.45 (d, $J = 7.8$ Hz, 6H), 7.28 (d, $J = 7.6$ Hz, 6H), 7.19 (d, $J = 7.8$ Hz, 6H), 4.82 (d, $J = 14.8$ Hz, 6H), 4.55 (d, $J = 14.6$ Hz, 6H), 0.86 (s, 54H), −0.04 (d, $J = 5.4$ Hz, 36H); IR (KBr) 3086, 2932, 2858, 2360, 1557, 1468, 1049, 805 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ε) 301 (4.98), 273 (4.88) nm; Found: C, 55.24; H, 5.29; F, 11.90; N, 6.55%. Calcd for $C_{120}H_{138}B_4Cu_4F_{16}N_{12}O_6Si_6$: C, 55.13; H, 5.32; F, 11.63; N, 6.43%.

Crystal Structure Determination. Single crystals of **CL7** were grown from dichloromethane by the slow diffusion of hexane vapor. Each single crystal was sealed into a glass capillary and mounted on a crystal goniometer. The X-ray diffraction data were collected on a Rigaku RAXIS-IV imaging area detector with graphite monochromated Mo-Kα radiation ($\lambda = 0.71070$ Å). Indexing was performed from 3 oscillations that were exposed for 8.0 minutes. The camera radius was 105.00 mm with the detector at the zero swing position, and readout was performed in the 0.100 mm pixel mode. A total of 40 data images (2.0 oscillation range) were collected, each being exposed for 15.0 minutes. The data were corrected for Lorentz and polarization effects. Calculations were carried out on an SGI Indy using the teXsan[19] crystallographic software package from Molecular Science Corporation. The structure was solved by direct methods of SIR92[20] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed in

Table 3. Crystallographic Data of **CL7**·CH_2Cl_2

Formula	$C_{70}H_{59}Cl_2Cu_3F_{18}N_9O_6P_3$
Fw	1818.73
Crystal size/mm	0.30 × 0.25 × 0.05
Crystal system	monoclinic
Space group	$P2_1/c$ (No. 14)
a/Å	13.797(2)
b/Å	21.054(4)
c/Å	27.27(2)
β/deg	101.693(3)
V/Å^3	7756(2)
Z	4
D_{calc}/g cm^{-3}	1.557
T/K	288
μ/cm^{-1}	10.45
$F(000)$	3672
$2\theta_{max}$/deg	55.1
No. of reflections measured	14846
No. of observed data ($I > 3.0\sigma(I)$)	10378
No. of variables	1000
Shift/Error	0.01
R	0.069
R_w	0.071

$R = \Sigma\|F_0| - |F_c\|/\Sigma|F_0|$, $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2}$; $w = 1/\sigma^2(|F_0|)$

calculated positions. The refinement of the structure was performed by full-matrix least-squares methods. Neutral atom scattering factors were taken from the literature.[21] The crystallographic data and structure refinement parameters are summarized in Table 3. Crystallographic data (excluding structure factors) for **CL7** have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 199007. Copies of the data can be obtained free of charge from the CCDC (12 Union Road, Cambridge CB2 1EZ, UK (http://www.ccdc.cam.ac.uk).

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