

Self-Assembly and Substituent Effect of Copper(I) Complexes with 1,2-Bis(2-pyridylethynyl)benzene Ligands

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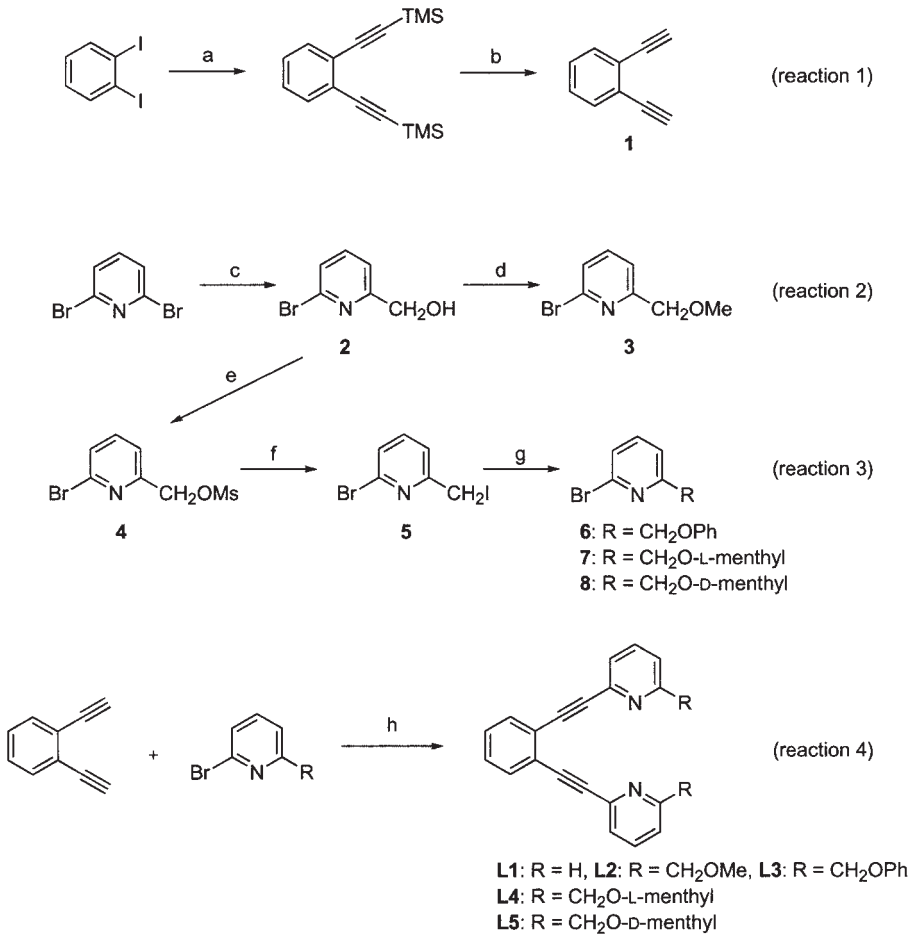
The reaction of 1,2-bis(2-pyridylethynyl)benzenes (**L1–L5**) with copper(I) ions proceeded smoothly to afford mononuclear copper(I) chelate complexes **CL1–CL3** or dinuclear copper(I) molecular rectangular boxes, **CL4** and **CL5**, in excellent yields, depending on the size of the substituent. If a ligand with a small substituent was used, the self-assembly of a mononuclear copper(I) chelate complex was achieved. If a ligand with a bulky substituent was used, the self-assembly of dinuclear copper(I) molecular rectangular boxes was achieved. The equilibrium between these two copper(I) complexes was also observed in solution.

The metal ion-assisted self-assembly of functionalized higher order supramolecular structures is currently of interest in the field of metallosupramolecular chemistry.[1] In metallosupramolecular chemistry, the self-assembly of defined species in thermodynamically controlled processes is achieved by the mixing of metal ions with appropriate organic ligands in solution. Therefore, various factors, such as the suitable design of ligands, preferred coordination geometries of the metals, and templating effects, play a pivotal role in the self-assembly process.[2,3] In our previous communication, we reported that the coordination of π-conjugated nitrogen ligands, 1,2-bis(2-pyridylethynyl)benzenes,[4] with copper(I) ion led to the self-assembly of mononuclear chelate complexes or dinuclear molecular rectangular boxes.[5,6] These previous reports suggest that the self-assembly of copper(I) complexes from 1,2-bis(2-pyridylethynyl)benzenes should depend on the size of the substituent of the ligand. Far less attention has been devoted to the substituent effect in the self-assembly of such a mononuclear chelate complex and a dinuclear molecular rectangular box, although many reports on the substituent effect in the self-assembly of metal complexes have been documented in the literature to date.[7] It was therefore expected that 1,2-bis(2-pyridylethynyl)benzenes should be one of the best ligands for investigating the substituent effect in the self-assembly of the copper(I) complex. We describe herein the self-assembly and substituent effects of copper(I) complexes from 1,2-bis(2-pyridylethynyl)benzenes in detail.

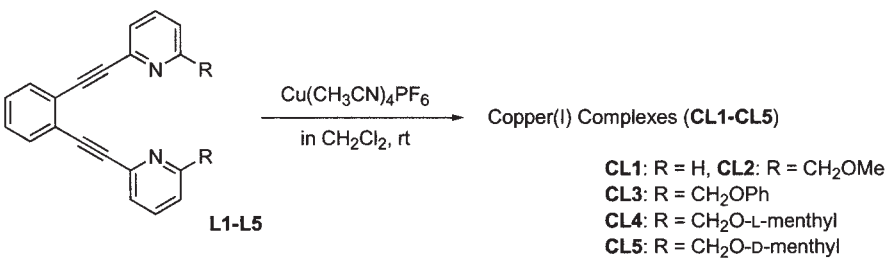
Results and Discussion

Preparation of the Ligands L1–L5. The synthesis of ligands **L1–L5** in this study is outlined in Scheme 1. 1,2-Bis(ethynyl)-benzene (**1**) was prepared according to a previously described procedure.[8] The reaction of the sodium salt of 2-bromo-6-(hydroxymethyl)pyridine (**2**),[9,10] which was prepared by treatment of **2** with sodium hydride in tetrahydrofuran (THF) at 0 °C, with methyl iodide in THF at 0 °C afforded 2-bromo-6-(methoxymethyl)pyridine (**3**) in 97% yield. Treatment of **2** with methanesulfonyl chloride in the presence of triethylamine and 4-(dimethylamino)pyridine in THF at −40 °C gave the mesylate **4** in 95% yield, and then displacement of the resulting mesyl group with iodide in acetone at 60 °C afforded the corresponding primary iodide **5** in 98% yield. The reaction of sodium salts of phenol, L-menthol, or D-menthol with iodide **5** at 0 °C gave the 6-(phenoxymethyl) **6**, 6-(L-menthyloxymethyl) **7**, and 6-(D-menthyloxymethyl) derivatives **8** in 93%, 99%, and 94% yields, respectively. This synthetic protocol allows the preparation of 2-bromopyridine derivatives with a variety of substituents at the 6-position. The cross-coupling reaction of 1,2-bis(ethynyl)benzene (**1**) with the corresponding 2-bromopyridine derivatives in the presence of a catalytic amount of tetrakis(triphenylphosphine)-palladium in diethylamine at 80 °C afforded the desired ligands **L1–L5** in 72%, 92%, 95%, 68%, and 72% yields, respectively. All ligands obtained were characterized by spectroscopy (NMR, IR, and FAB mass) and elemental analysis.

Self-Assembly of Copper(I) Complexes. We first examined the coordination of the ligand **L2** with the copper(I) ion. The reaction of **L2** with an equimolar quantity of $[Cu(CH_3CN)_4]PF_6$[11] 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 **CL2** was obtained as yellow blocks in 90% yield (Scheme 2). The ^{1}H NMR spectra of **CL2** in dichloromethane-d_2 solution consisted of a simple pattern of peaks corresponding to **L2**, indicative of the formation of a symmetric species (Fig. 1). 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 **CL2** were shifted relative to those involved in **L2**. In particular, the proton signal (H_d) of the pyridine ring ($\Delta\delta = 0.38$) is shifted downfield relative to that of the free ligand **L2**. The UV electronic spectra of **CL2** displayed a new absorption at approximately 360 nm, which was assigned to a metal-to-ligand charge-transfer band (Fig. 2a). The change in absorbance analyzed by the mole ratio method at 358 nm showed a linear dependence on the amount of copper(I) salt added up to an approximately 1:1 **L2**:copper(I) ratio (Fig. 2b). This result indicates that a $[Cu(\mathbf{L2})]^+$ composition is generated. Further-



Scheme 1. Preparation of the ligands (**L1**–**L5**). *Reagents and conditions*: (a) TMSacetylene, $PdCl_2(PPh_3)_2$, CuI, piperidine, rt, 95%. (b) TBAF, THF–H_2O, 0 °C to rt, 83%. (c) (1) *n*-BuLi, THF, −78 °C, (2) DMF, THF, −78 °C, (3) $NaBH_4$, THF, 0 °C, 87%. (d) (1) NaH, THF, 0 °C, (2) MeI, THF, 0 °C, 97%. (e) MsCl, Et_3N, DMAP, THF, −40 °C, 95%. (f) NaI, acetone, 60 °C, 98%. (g) PhONa, THF, 0 °C, 93% (for **6**), sodium L-menthoxide, THF, 0 °C, 99% (for **7**), or sodium D-menthoxide, THF, 0 °C, 94% (for **8**). (h) $Pd(PPh_3)_4$, Et_2NH, 80 °C, 72% (for **L1**), 92% (for **L2**), 95% (for **L3**), 68% (for **L4**), and 72% (for **L5**).



Scheme 2. Synthesis of the copper(I) complexes (**L1**–**L5**). Yield: 87% (for **CL1**), 90% (for **CL2**), 100% (for **CL3**), 85% (for **CL4**), and 88% (for **CL5**).

more, based on FAB mass spectroscopy and elemental analysis, the molecular formula of **CL2** was determined to be [Cu(**L2**)](PF_6). Other copper(I) complexes (**CL1** ([Cu(**L1**)](PF_6)), **CL3** ([Cu(**L3**)](PF_6)), **CL4** ([Cu_2(**L4**)$_2$](PF_6)$_2$), and **CL5** ([Cu_2(**L5**)$_2$](PF_6)$_2$)) were also obtained in a similar manner in 87%, 100%, 85%, and 88% yields, respectively. Figure 3 shows the circular dichroism spectra of **CL4** and **CL5**, respectively. The spectra are mirror images of each other. Additionally, a significant change in the optical rotations of the complexes in chloroform (**CL4**, $[\alpha]_D$ −446.9° (*c* 1.62); **CL5**, $[\alpha]_D$ +418.4° (*c* 1.47)) implies that the reaction of ligands **L4** and **L5** with the copper(I) ions proceeded enantioselectively to afford enantiomerically pure complexes. The generation of dinuclear copper(I) complexes **CL4** and **CL5** implies that the substituent effect of the ligand plays an important role in the self-assembly of the copper(I) complex. Thus, we can imagine that when a ligand with a less bulky substituent is used, a mononuclear copper(I) complex is obtained, and when a ligand with a bulky subsitutent is used, a dinuclear copper(I) complex is obtained.

Structure of the Copper(I) Complexes. We attempted to

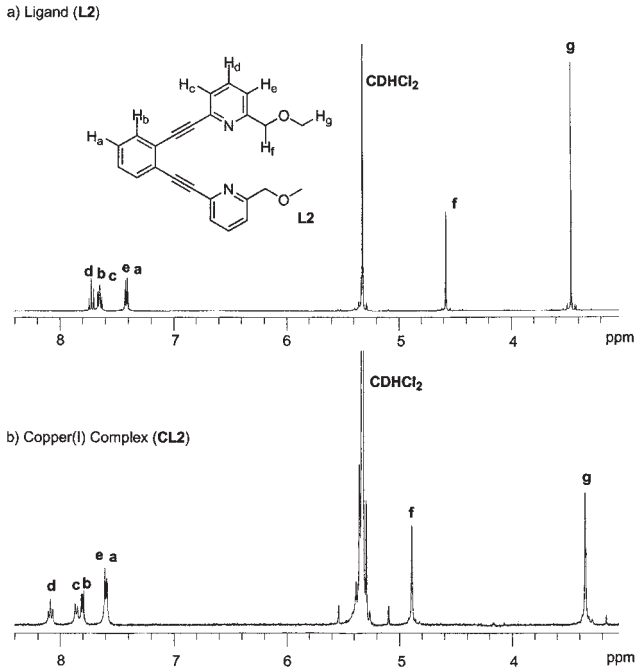


Fig. 1. The ^{1}H NMR spectra (400 MHz, CD_2Cl_2) of (a) the ligand (**L2**) and (b) the copper(I) complex (**CL2**).

prepare single crystals of complexes to investigate the structure of the copper(I) complexes obtained in this study by X-ray crystallography. Although we could not obtain single crystals of **CL1** and **CL2** due to their poor crystallinity, the conversion of the counter ion (PF_6^-) of copper(I) complex **CL2** to perchlorate (ClO_4^-) enabled us to prepare single crystals of copper(I) complex with ClO_4^- (**CL2′**). X-ray quality single crystals of **CL2′**, **CL3**, **CL4**, and **CL5** were obtained by recrystallization from CH_2Cl_2 by the slow diffusion of hexane vapor (for **CL2′**), acetone (for **CL3**), and methanol (for **CL4** and **CL5**), respectively. The crystal structures of **CL2′** and **CL3** are shown in Fig. 4.[12–14] The copper(I) complexes **CL2′** and **CL3** consist of one ligand, one two-coordinate copper(I) ion, and one counter ion. In the case of **CL2′**, the ligand coordinates copper(I) ions in a *trans*-chelating mode (Fig. 4a). The average dihedral angle between the aromatic rings in **CL2′** is 3.63°, indicative of the formation of a planar complex. The bond length of Cu–N is 1.935 Å and the bite angle of N–Cu–N is 170.28(7)°. **CL2′** is therefore a mononuclear copper(I) chelate complex. The ClO_4^- anion adopts a position nearly perpendicular to the N–Cu–N axis. The distance between the copper(I) ion and the adjacent oxygen atom of the ClO_4^- anion is 2.43 Å, indicative of the presence of a relatively strong interaction. The crystal structure of the cation of **CL3** also had a planar structure similar to that of **CL2′** (Fig. 4b), indicating that, in the case of our complexes, no difference between PF_6^- and ClO_4^- affects the cation structure. The distance between the copper(I) ion and the hexafluorophosphate anion (PF_6^-) of **CL3** is 2.8 Å, implying a weak interaction of PF_6^- with the copper(I) ion. The two aromatic rings in the terminal substituent of **L3** are almost perpendicular (92.78°) to each other. Furthermore, based on the ^{1}H NMR spectrum and elemental analysis of **CL1**, it can be determined that **CL1** is also a mononuclear copper(I) chelate complex. In contrast, the structural analysis showed **CL4** and **CL5** to be $[Cu_2(\mathbf{L4})_2]$-

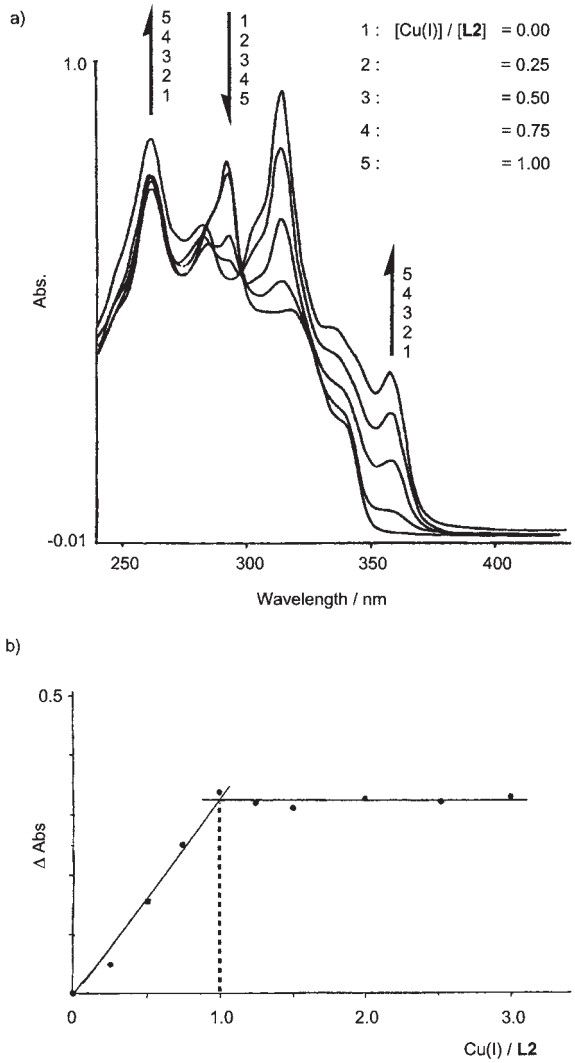


Fig. 2. (a) Spectrophotometric titration of **L2** with $Cu(CH_3CN)_4PF_6$ in CH_2Cl_2. (b) The changes in absorbance analyzed by the mole ratio methods at 358 nm.

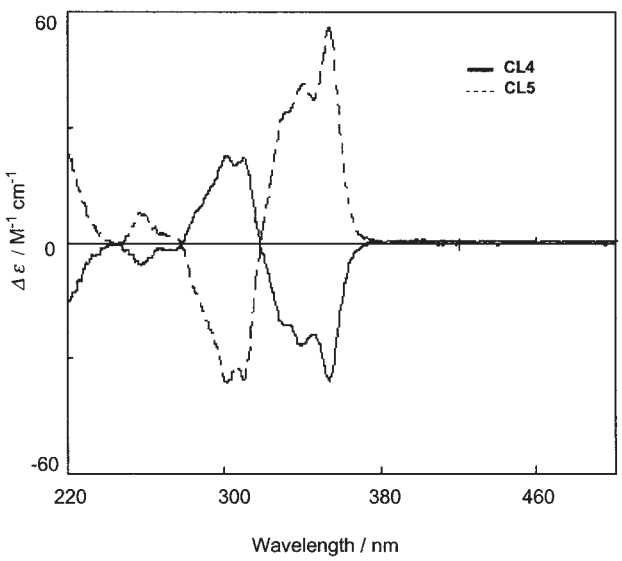


Fig. 3. CD spectra of **CL4** and **CL5** in chloroform.

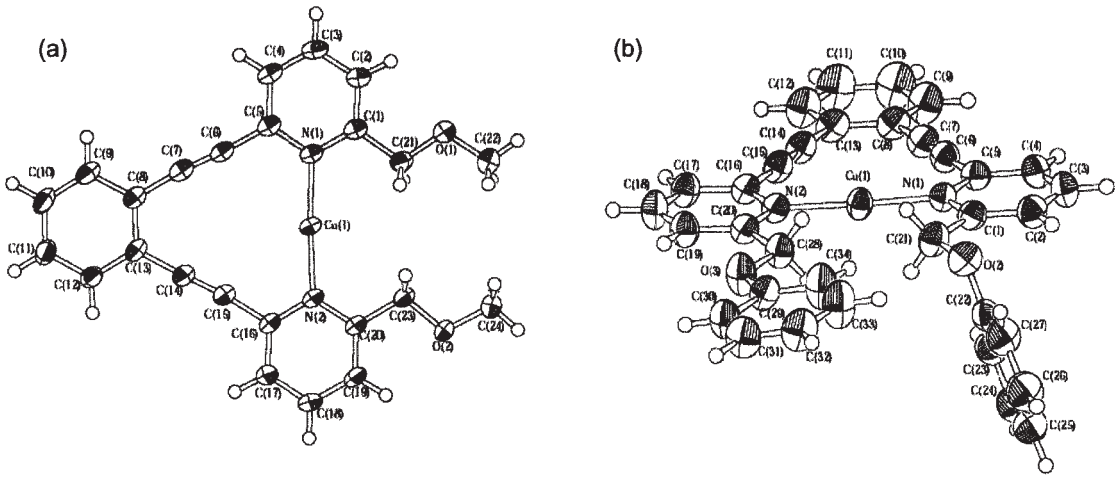


Fig. 4. ORTEP representations of (a) **CL2′** and (b) **CL3**. Counter ions are omitted for clarity.

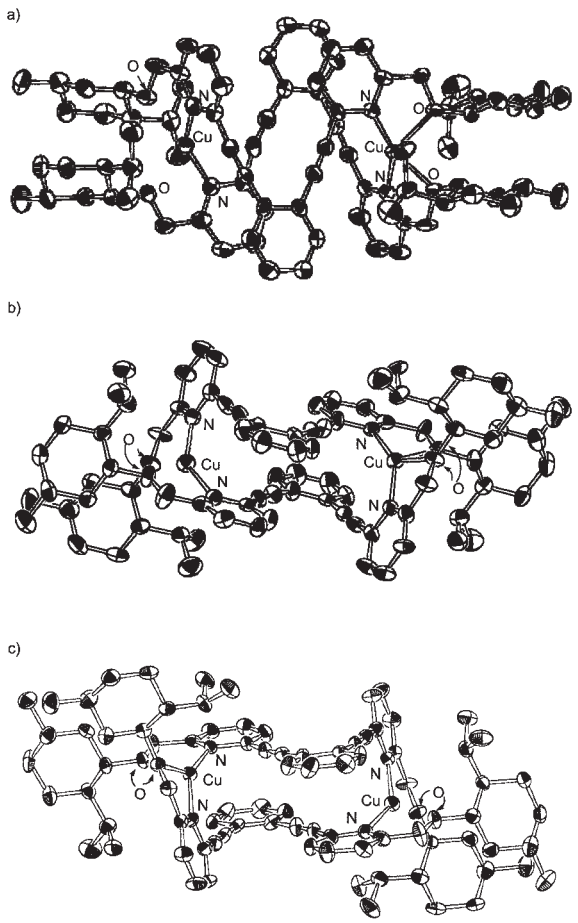


Fig. 5. ORTEP representations of **CL4** and **CL5** (a) from a top view of **CL4**, (b) from a side view of **CL4**, and (c) from a side view of **CL5**. Counter ions and hydrogen atoms are omitted for clarity.

$(PF_6)_2$[15] and $[Cu_2(\mathbf{L5})_2](PF_6)_2$[16] (Fig. 5). As shown in Fig. 5, **CL4** consists of two copper(I) ions, two ligands, and two uncoordinated counterions, and is structured as a dinuclear copper(I) molecular rectangular box. The structure of **CL5** is a mirror image of **CL4**. The crystal system of **CL4** and **CL5** was determined to be triclinic $P1$, which is in a chiral space group. Each copper(I) ion of **CL4** has a distorted tetrahedral (N_2O_2) coordination. The bond length between the copper(I) ion and the nitrogen atom of the pyridine ring is in the range of 1.91–2.03 Å, and the bond angles between N–Cu(I)–N are 138.4° and 142.7°. A slight bending of the triple bond (bond angle: 173°) is also observed. Oxygen atoms weakly coordinate to the copper(I) ion (bond length: 2.25 Å). The two ligands of **CL4** are stacked coplanar above each other, with an interplane distance of approximately 3.5 Å, indicative of the presence of a π–π interaction. In one ligand of **CL4**, the pyridyl and the remaining 1-ethynyl-2-(2-pyridylethynyl)phenyl binding domains are twisted with respect to each other (average twist angle: 84.5°); the coordination of the two ligands with the two copper(I) ions therefore produces a hollow cavity. This finding clearly demonstrates that the steric hindrance between the terminal bulky substituents in the ligand has a large effect on the self-assembly of the copper(I) complex.

DSC Traces for the Thermal Cyclizations of Ligand and Copper(I) Complex. The ligands and the copper(I) complexes in this study possess an endiyne skeleton. To probe the possible thermal reactivity of our system, we examined their behavior by differential scanning calorimetry (DSC). Figure 6 illustrates the DSC traces for the thermal cyclization of the ligand **L4** and the copper(I) complexes **CL1** and **CL4**. Ligand **L4** exhibits a sharp endothermic peak at about 118 °C, followed by a broad exothermic peak at above 300 °C. On the other hand, complex **CL1** exhibits only a broad exothermic peak at above 300 °C, and complex **CL4** exhibits a sharp endothermic peak at about 250 °C, followed by a broad exothermic peak at about 275 °C. This indicates that ligand **L4** and mononuclear chelate complex **CL1** are more thermally stable than dinuclear complex **CL4**, and that the thermal cyclization of **CL4** may proceed between two ligands which compose complex **CL4**.

Behavior of the Copper(I) Complexes in Solution. It was thought that, from a structural point of view, the concentration-dependent behavior of the copper(I) complexes mentioned above should be observed in a particular copper(I) complex. To investigate this point, we measured the ^{1}H NMR spectra of **CL3** at a dilute concentration (0.98 mM) (1 M = 1 mol dm^{-3}) and a higher concentration (16 mM). As shown in Fig. 7, The ^{1}H NMR

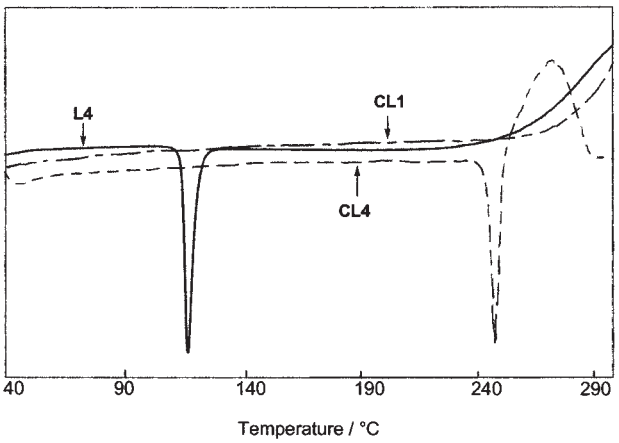


Fig. 6. DSC traces for the thermal cyclization of **L4**, **CL1**, and **CL4**.

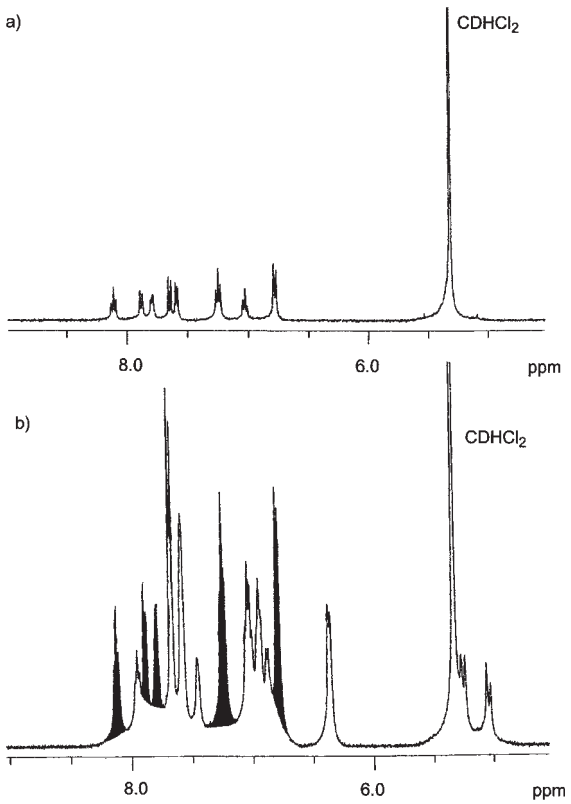


Fig. 7. The ^{1}H NMR spectra of **CL3** (a) at a dilute concentration (0.98 mM) and (b) at a higher concentration (16 mM).

measurement of **CL3** at a higher concentration resulted in the appearance of new peaks, which implies the formation of a copper(I) complex different from **CL3**. This new complex should be a dinuclear copper(I) complex. This behavior was also observed in **CL2**. To clarify the concentration-structure relationship of copper(I) complexes **CL2** and **CL3**, we examined the abundance of complexes under several concentration conditions (Fig. 8). In the case of **CL3**, the abundance of the mononuclear copper(I) complex was found to decrease with increases in the concentration, and a dinuclear copper(I) complex is then

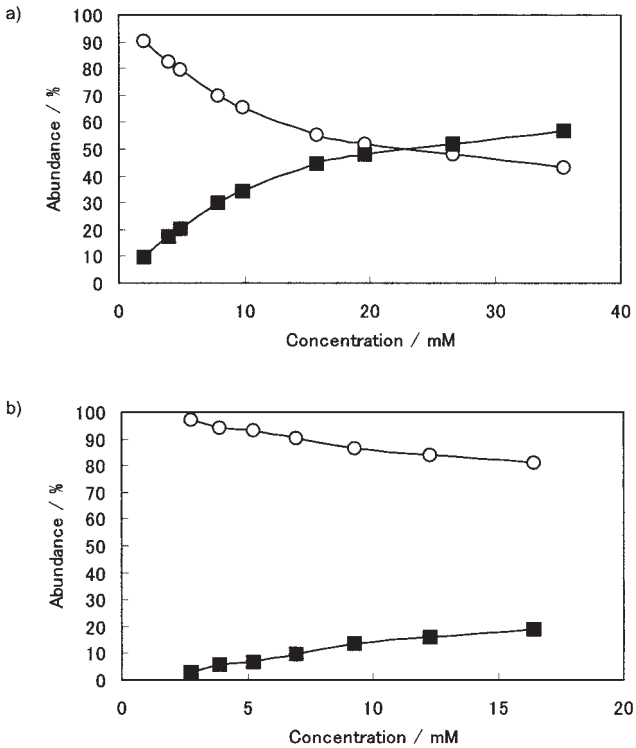


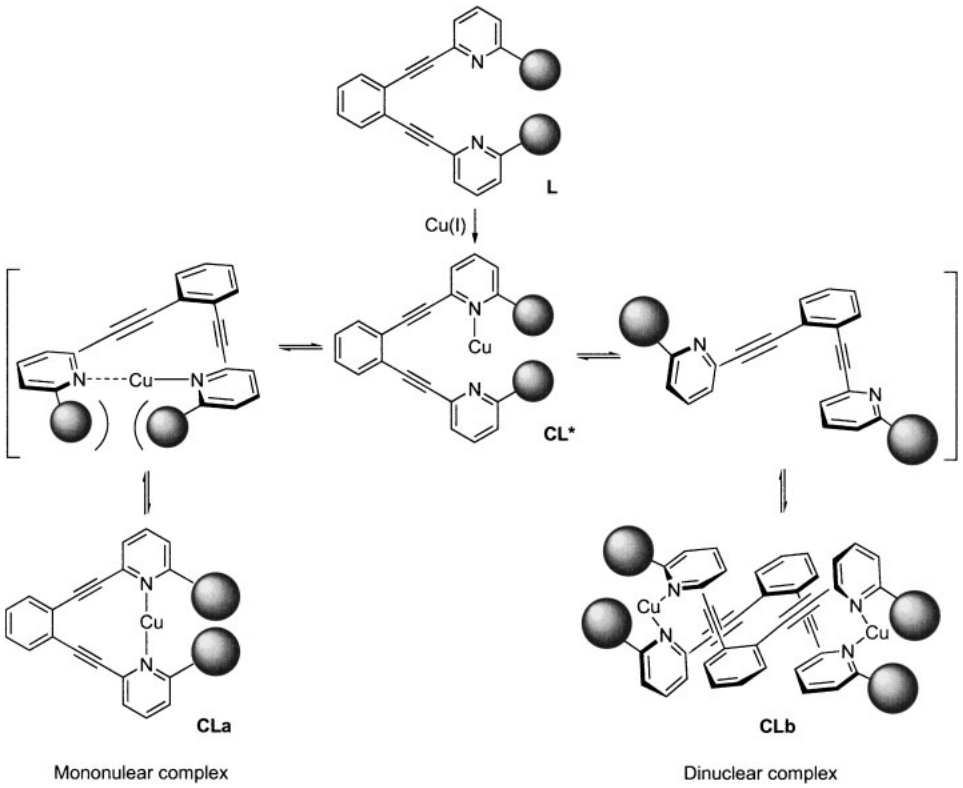
Fig. 8. The abundance of complexes (a) **CL3** and (b) **CL2** under several concentration conditions in CH_2Cl_2. The abundance of the mononuclear complex and the dinuclear copper(I) complex, are marked with a white circle and a black square, respectively.

generated as the main product at concentrations above that of a 22 mM solution of **CL3** (Fig. 8a). **CL2** showed behavior similar to that of **CL3**, though the main product was a mononuclear copper(I) complex at concentrations below 16 mM.[17] On the other hand, no new peaks were observed in the ^{1}H NMR spectra of **CL1** at concentrations below 4.2 mM.[18] In the case of **CL4** and **CL5**, no new peaks were observed at concentrations in the range of 0.35–20 mM.

A proposed mechanism for the self-assembly of copper(I) complexes in this study is presented in Scheme 3. The coordination of the ligand (**L**) with the copper(I) ion first gives a monodentate copper(I) complex (**CL***) as a reaction intermediate. If the ligand in **CL*** has a small substituent, a chelate-closing reaction occurs immediately to give a mononuclear copper(I) chelate complex (**CLa**). If the ligand in **CL*** has a bulky substituent, steric hindrance between the two substituents prevents a mononuclear copper(I) chelate complex from being generated. Consequently, dimerization of **CL*** occurs to afford a dinuclear copper(I) complex **CLb**. If a ligand with a substituent less bulky in size is used, two types of copper(I) complexes, **CLa** and **CLb**, are in an equilibrium state, depending on the concentration of the reaction solution, and then the more thermodynamically stable complex would be obtained exclusively.

Conclusion

In conclusion, we have demonstrated that the coordination of 1,2-bis(2-pyridylethynyl)benzenes with copper(I) ions proceeds



Scheme 3. A proposed mechanism for the self-assembly of the copper(I) complexes (**CLa** and **CLb**) in this study.

smoothly to yield mononuclear copper(I) chelate complexes or dinuclear copper(I) molecular rectangular boxes in excellent yields, depending on the size of the substituent. Metal complexes interconverting between monomers and self-assembled oligomers by an input of external information would provide us with a new material for the further development of metallosupramolecular chemistry.

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 when necessary.[19] 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). The 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. DSC curves were recorded on a SHIMADZU DSC-50 differential scanning calorimeter. Column chromatography was performed on Merck silica gel 60. 1,2-Bis(ethynyl)benzene (**1**)[8] and 2-bromo-6-(hydroxymethyl)pyridine (**2**)[9,10] were prepared according to the literature procedure.

2-Bromo-6-(methoxymethyl)pyridine (3).[10] To a suspension of sodium hydride (60% in mineral oil, 0.729 g, 30.9 mmol) in THF (30 mL) was added dropwise a solution of 2-bromo-6-(hydroxymethyl)pyridine (**2**) (4.87 g, 25.9 mmol) in THF (30 mL) at 0 °C. The reaction mixture was stirred at the same temperature for 1 h, and then methyl iodide (5.0 mL, 80.3 mmol) was added. After being stirred at the same temperature for 1 h, the reaction mixture was quenched with cold saturated aqueous NH_4Cl and extracted with AcOEt. The organic layer was washed with H_2O and brine, successively, 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 **3** (5.42 g, 97%) as a pale yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (t, J = 7.7 Hz, 1H), 7.41 (d, J = 7.8 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 4.56 (s, 2H), 3.48 (d, 3H).

2-Bromo-6-(methanesulfonylmethyl)pyridine (4). To a solution of 2-bromo-6-(hydroxymethyl)pyridine (**2**) (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 with saturated aqueous $NaHCO_3$, H_2O, and brine, successively, and then dried over anhydrous $MgSO_4$. After removal of the solvent, an oily residue was purified by column chromatography (silica gel, hexane–AcOEt) to give **4** (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); IR (neat) 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%.

2-Bromo-6-(iodomethyl)pyridine (5). To a solution of **4** (3.93 g, 14.8 mmol) in acetone (150 mL) was added NaI (8.87 g, 59.2 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 with saturated aqueous $Na_2S_2O_3$, H_2O, and brine, successively, 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 **5** (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); 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%.

2-Bromo-6-(phenoxymethyl)pyridine (6). To a suspension of sodium hydride (60% in mineral oil, 0.504 g, 21.0 mmol) in THF (25 mL) was added dropwise a solution of phenol (1.83 g, 19.4 mmol) in THF (25 mL) at 0 °C. The reaction mixture was stirred at the same temperature for 0.5 h, and then a solution of **5** (2.50 g, 8.39 mmol) in THF (25 mL) was added. After being stirred at room temperature for 2 h, the reaction mixture was quenched with cold saturated aqueous NH_4Cl and extracted with AcOEt. The organic layer was washed with H_2O and brine, successively, and then dried over anhydrous $MgSO_4$. After removal of the solvent, the oily residue was purified by column chromatography (silica gel, hexane–C_6H_6) to give **6** (2.07 g, 93%) as colorless needles: mp 63.2–63.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (t, J = 7.7 Hz, 1H), 7.51 (d, J = 6.8 Hz, 1H), 7.42 (d, J = 7.6 Hz, 1H), 7.30 (t, 2H), 6.99 (t, 1H), 6.96 (d, 2H), 5.19 (s, 2H); IR (KBr) 3040, 2905, 2860, 1600, 1555, 1500, 1445, 1405, 1250, 1075, 790 cm^{-1}; FABMS (NBA) m/z 265 [(M + H)$^+$]; Found: C, 54.31; H, 3.70; N, 5.20; Br, 30.11%. Calcd for $C_{12}H_{10}BrNO$: C, 54.57; H, 3.82; N, 5.30; Br, 30.25%.

2-Bromo-6-(L-menthyloxymethyl)pyridine (7). This compound was prepared from **5** and L-menthol according to the method used for the preparation of **6**. Colorless oil; yield 99%; $[\alpha]_D$ −73 (c 1.74, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, J = 7.6, 7.8 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.33 (d, J = 7.8 Hz, 1H), 4.74 (d, J = 13.9 Hz, 1H), 4.49 (d, J = 13.9 Hz, 1H), 3.21 (dt, J = 4.1, 10.5 Hz, 1H), 2.26 (tdd, J = 2.7, 6.8, 10.5 Hz, 1H), 2.14 (br d, J = 7.1 Hz, 1H), 1.70–1.58 (m, 2H), 1.44–1.26 (m, 2H), 1.05–0.77 (m, 9H), 0.73 (d, J = 7.1 Hz, 3H); IR (neat) 2960, 2930, 2850, 1590, 1560, 1420, 1130, 990, 850, 795 cm^{-1}; FABMS (NBA) m/z 327 [(M + H)$^+$]; Found: C, 58.97; H, 7.30; N, 4.11; Br, 24.50%. Calcd for $C_{16}H_{24}BrNO$: C, 58.91; H, 7.41; N, 4.29; Br, 24.49%.

2-Bromo-6-(D-menthyloxymethyl)pyridine (8). This compound was prepared from **5** and D-menthol according to the method used for the preparation of **6**. Colorless oil; yield 94%; $[\alpha]_D$ +63.9 (c 2.21, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, J = 7.6, 7.8 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.33 (d, J = 7.8 Hz, 1H), 4.74 (d, J = 13.9 Hz, 1H), 4.49 (d, J = 13.9 Hz, 1H), 3.21 (dt, J = 4.1, 10.5 Hz, 1H), 2.26 (tdd, J = 2.7, 6.8, 10.5 Hz, 1H), 2.14 (br d, J = 7.1 Hz, 1H), 1.70–1.58 (m, 2H), 1.44–1.26 (m, 2H), 1.05–0.77 (m, 9H), 0.73 (d, J = 7.1 Hz, 3H); IR (neat) 2960, 2930, 2850, 1590, 1560, 1420, 1130, 990, 850, 795 cm^{-1}; FABMS (NBA) m/z 327 [(M + H)$^+$]; Found: C, 58.99; H, 7.35; N, 4.18; Br, 24.52%. Calcd for $C_{16}H_{24}BrNO$: C, 58.91; H, 7.41; N, 4.29; Br, 24.49%.

1,2-Bis(2-pyridylethynyl)benzene (L1).[4a] To a mixture of 2-bromopyridine (0.571 g, 3.61 mmol), tetrakis(triphenylphosphine)-palladium (0.060 g, 0.052 mmol) and diethylamine (10 mL) was added dropwise a solution of 1,2-bis(ethynyl)benzene **1** (0.200 g, 1.59 mmol) in diethylamine (5 mL) at room temperature. After being stirred at 80 °C for 12 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 oily residue was dissolved with AcOEt, and the resulting solution was washed with saturated aqueous NH_4Cl, H_2O, and brine, successively, and then dried over $MgSO_4$. After removal of the solvent, the oily residue was purified by column chromatography (silica gel, AcOEt–C_6H_6) to give **L1** (0.320 g, 72%) as colorless plates: mp 112.8–114.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (dt, J = 1.2, 4.9 Hz, 2H), 7.70–7.67 (m, 4H), 7.66 (dd, J = 5.8, 3.4 Hz, 2H), 7.38 (dd, J = 5.8, 3.3 Hz, 2H), 7.26 (ddd, J = 6.3, 4.9, 2.4 Hz, 2H); IR (KBr) 3060, 2220, 1580, 1485, 755, 735 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ε) 315 (4.36), 289 (4.56), 261 (4.57) nm; FABMS (NBA) m/z 281 [(M + H)$^+$]; Found: C, 85.38; H, 4.31; N, 9.76%. Calcd for $C_{20}H_{12}N_2$: C, 85.69; H, 4.31; N, 9.99%.

1,2-Bis[(6-methoxymethyl-2-pyridyl)ethynyl]benzene (L2). This compound was prepared from **1** and **3** according to the method used for the preparation of **L1**. Pale yellow solids; yield 92%; mp 38.8–41.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (t, J = 7.8 Hz, 2H), 7.65 (dd, J = 5.8, 3.2 Hz, 2H), 7.62 (d, J = 7.8 Hz, 2H), 7.43 (d, J = 7.8 Hz, 2H), 7.37 (dd, J = 5.7, 3.3 Hz, 2H), 4.63 (s, 4H), 3.50 (s, 6H); IR (KBr) 2820, 2210, 1580, 1570, 1485, 1455, 1115, 800, 760 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ε) 318 (4.34), 293 (4.55), 262 (4.53) nm; FABMS (NBA) m/z 369 [(M + H)$^+$]; Found: C, 78.35; H, 5.41; N, 7.62%. Calcd for $C_{24}H_{20}N_2O_2$: C, 78.24; H, 5.47; N, 7.60%.

1,2-Bis[(6-phenoxymethyl-2-pyridyl)ethynyl]benzene (L3). This compound was prepared from **1** and **6** according to the method used for the preparation of **L1**. Colorless needles; yield 95%; mp 122.1–122.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, J = 6.0, 3.2 Hz, 2H), 7.68–7.64 (m, 4H), 7.50 (dd, J = 7.1, 2.0 Hz, 2H), 7.39 (dd, J = 5.7, 3.3 Hz, 2H), 7.30 (t, J = 8.1 Hz, 4H), 6.99–6.96 (m, 6H), 5.25 (s, 4H); IR (KBr) 3055, 2900, 2860, 2210, 1600, 1570, 1500, 1445, 1245, 1055, 795, 765 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ε) 319 (4.05), 293 (4.27), 263 (4.23) nm; FABMS (NBA) m/z 493 [(M + H)$^+$]; Found: C, 82.69; H, 4.71; N, 5.81%. Calcd for $C_{34}H_{24}N_2O_2$: C, 82.91; H, 4.91; N, 5.69%.

1,2-Bis[(6-L-menthoxymethyl-2-pyridyl)ethynyl]benzene (L4). This compound was prepared from **1** and **7** according to the method used for the preparation of **L1**. Colorless plates; yield 68%; mp 114.7–115.4 °C; $[\alpha]_D$ −69.1 (c 1.94, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (t, J = 7.7 Hz, 2H), 7.65 (dd, J = 5.5, 3.5 Hz, 2H), 7.58 (d, J = 7.1 Hz, 2H), 7.49 (d, J = 7.3 Hz, 2H), 7.36 (dd, J = 5.9, 3.4 Hz, 2H), 4.82 (d, J = 13.7 Hz, 2H), 4.59 (d, J = 13.7 Hz, 2H), 3.26 (dt, J = 4.0, 10.6 Hz, 2H), 2.32 (dsp, J = 2.7, 7.0 Hz, 2H), 2.20 (brd, J = 12.1 Hz, 2H), 1.69–1.64 (m, 4H), 1.44–1.31 (m, 4H), 1.06–0.83 (m, 6H), 0.94 (d, J = 2.7 Hz, 6H), 0.92 (d, J = 3.2 Hz, 6H), 0.76 (d, J = 7.1 Hz, 6H); IR (KBr) 2955, 2920, 2210, 1565, 1455, 1115, 765 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ε) 319 (4.39), 293 (4.61), 262 (4.57) nm; FABMS (NBA) m/z 617 [(M + H)$^+$]; Found: C, 81.55; H, 8.52; N, 4.39%. Calcd for $C_{42}H_{52}N_2O_2$: C, 81.78; H, 8.50; N, 4.54%.

1,2-Bis[(6-D-menthoxymethyl-2-pyridyl)ethynyl]benzene (L5). This compound was prepared from **1** and **8** according to the method used for the preparation of **L1**. Colorless plates; yield 72%; mp 114.7–115.4 °C; $[\alpha]_D$ +66.9 (c 1.57, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (t, J = 7.7 Hz, 2H), 7.65 (dd, J = 5.5, 3.5 Hz, 2H), 7.58 (d, J = 7.1 Hz, 2H), 7.49 (d, J = 7.3 Hz, 2H), 7.36 (dd, J = 5.9, 3.4 Hz, 2H), 4.82 (d, J = 13.7 Hz, 2H), 4.59 (d, J = 13.7 Hz, 2H), 3.26 (dt, J = 4.0, 10.6 Hz, 2H), 2.32 (dsp, J = 2.7, 7.0 Hz,

2H), 2.20 (brd, $J = 12.1$ Hz, 2H), 1.69–1.64 (m, 4H), 1.44–1.31 (m, 4H), 1.06–0.83 (m, 6H), 0.94 (d, $J = 2.7$ Hz, 6H), 0.92 (d, $J = 3.2$ Hz, 6H), 0.76 (d, $J = 7.1$ Hz, 6H); IR (KBr) 2955, 2920, 2210, 1565, 1455, 1115, 765 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ε) 319 (4.39), 293 (4.61), 262 (4.57) nm; FABMS (NBA) m/z 617 [$(M + H)^+$]; Found: C, 81.80; H, 8.51; N, 4.33%. Calcd for $C_{42}H_{52}N_2O_2$: C, 81.78; H, 8.50; N, 4.54%.

Copper(I) Complex CL1: [Cu(L1)](PF$_6$). To a solution of tetrakis(acetonitrile)copper(I) hexafluorophosphate (0.293 g, 0.786 mmol) in dichloromethane (30 mL) was added dropwise a solution of **L1** (0.218 g, 0.778 mmol) in dichloromethane (6.0 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 crude yellow crystals. Recrystallization of the crude crystals from dichloromethane–hexane gave the pure complex **CL1** (0.340 g, 87%) as yellow powders: mp >300 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.96 (d, $J = 5.4$ Hz, 2H), 8.00 (t, $J = 7.8$ Hz, 2H), 7.81 (d, $J = 8.0$ Hz, 2H), 7.63 (dd, $J = 5.7$, 3.2 Hz, 2H), 7.63 (dd, $J = 7.8$, 5.4 Hz, 2H), 7.44 (dd, $J = 5.7$, 3.3 Hz, 2H); IR (KBr) 3120, 2225, 1600, 1495, 840, 765 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ε) 354 (4.36), 331 (4.43), 310 (4.74), 277 (4.61), 256 (4.61) nm; FABMS (NBA) m/z 343 [$(M - PF_6)^+$]; Found: C, 49.35; H, 2.69; N, 5.59; F,23.22; P, 6.22%. Calcd for $C_{20}H_{12}CuF_6N_2P$: C, 49.14; H, 2.47; N, 5.73; F, 23.32; P, 6.34%.

Copper(I) Complex CL2: [Cu(L2)](PF$_6$). This compound was synthesized from **L2** and $Cu(CH_3CN)_4(PF_6)$ according to the method used for the preparation of **CL1**. Yellow solids; yield 90%; mp 180 °C (dec); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.08 (t, $J = 7.8$ Hz, 2H), 7.85 (d, $J = 7.8$ Hz, 2H), 7.80 (dd, $J = 5.8$, 3.3 Hz, 2H), 7.61 (d, $J = 8.0$ Hz, 2H), 7.59 (dd, $J = 5.9$, 3.2 Hz, 2H), 4.89 (s, 4H), 3.36 (s, 6H); IR (KBr) 2940, 2835, 2215, 1600, 1565, 1485, 1455, 1115, 840, 800, 770 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ε) 358 (4.12), 333 (4.23), 314 (4.54), 282 (4.39), 261 (4.45) nm; FABMS (NBA) m/z 431 [$(M - PF_6)^+$]; Found: C, 49.70; H, 3.42; N, 4.78; F, 19.69; P, 5.24%. Calcd for $C_{24}H_{20}CuF_6N_2O_2P$: C, 49.96; H, 3.49; N, 4.86; F, 19.76; P, 5.37%.

Copper(I) Complex CL3: [Cu(L3)](PF$_6$). This compound was synthesized from **L3** and $Cu(CH_3CN)_4(PF_6)$ according to the method used for the preparation of **CL1**. Yellow blocks; yield 100%; mp 100.6–101.9 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.13 (t, $J = 7.8$ Hz, 2H), 7.90 (d, $J = 7.8$ Hz, 2H), 7.80 (dd, $J = 5.8$, 3.2 Hz, 2H), 7.65 (d, $J = 7.8$ Hz, 2H), 7.60 (dd, $J = 5.8$, 3.2 Hz, 2H), 7.25 (t, 4H), 7.03 (t, 4H), 6.77 (d, 4H), 5.31 (s, 2H); IR (KBr) 3075, 2935, 2210, 1600, 1570, 1490, 1455, 1220, 1035, 840, 800, 755 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ε) 361 (4.09), 337 (4.23), 316 (4.57), 278 (4.40), 263 (4.47) nm; FABMS (NBA) m/z 555 [$(M - PF_6)^+$]; Found: C, 58.04; H, 3.20; N, 4.28; F, 16.09; P, 4.30%. Calcd for $C_{34}H_{24}CuF_6N_2O_2P$: C, 58.25; H, 3.45; N, 4.00; F, 16.26; P, 4.42%.

Copper(I) Complex CL4: [Cu$_2$(L4)$_2$](PF$_6$)$_2$. This compound was synthesized from **L4** and $Cu(CH_3CN)_4(PF_6)$ according to the method used for the preparation of **CL1**. Yellow blocks; yield 85%; mp 240 °C (dec); $[\alpha]_D$ −446.9 (c 1.62, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.10 (t, $J = 7.8$ Hz, 4H), 7.84 (d, $J = 7.8$ Hz, 4H), 7.80 (dd, $J = 5.6$, 3.4 Hz, 4H), 7.63 (d, $J = 7.6$ Hz, 4H), 7.59 (dd, $J = 5.7$, 3.3 Hz, 4H), 5.20 (d, $J = 14.6$ Hz, 4H), 4.82 (d, $J = 14.6$ Hz, 4H), 3.06 (dt, $J = 4.0$, 10.4 Hz, 4H), 2.45 (dsp, $J = 2.3$, 7.0 Hz, 4H), 2.18 (brd, $J = 11.5$ Hz, 4H), 1.60 (brd, $J = 11.0$ Hz, 4H), 1.52 (brd, $J = 9.8$ Hz, 4H), 1.38–1.22 (br, 8H), 1.11–1.05 (brt, $J = 10.8$ Hz, 12H), 0.92 (d, $J = 6.6$ Hz, 12H), 0.90–0.75 (m, 12H), 0.62 (d, $J = 7.1$ Hz, 12H); IR (KBr) 2955, 2925, 2215, 1565, 1455, 1085, 840, 770 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ε) 358 (4.52), 334 (4.62), 314 (4.96), 282 (4.77), 261 (4.87) nm; FABMS (NBA) m/z 1505 [$(M - PF_6)^+$]; Found: C, 61.13; H, 6.26; N, 3.46; F, 13.77; P, 3.69%. Calcd for $C_{84}H_{104}Cu_2F_{12}N_4O_4P_2$: C, 61.12; H, 6.35; N, 3.39; F, 13.81; P, 3.75%.

Copper(I) Complex CL5: [Cu$_2$(L5)$_2$](PF$_6$)$_2$. This compound was synthesized from **L5** and $Cu(CH_3CN)_4(PF_6)$ according to the method used for the preparation of **CL1**. Yellow blocks; yield 88%; mp 241 °C (dec); $[\alpha]_D$ −418.4 (c 1.47, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.10 (t, $J = 7.8$ Hz, 4H), 7.84 (d, $J = 7.8$ Hz, 4H), 7.80 (dd, $J = 5.6$, 3.4 Hz, 4H), 7.63 (d, $J = 7.6$ Hz, 4H), 7.59 (dd, $J = 5.7$, 3.3 Hz, 4H), 5.20 (d, $J = 14.6$ Hz, 4H), 4.82 (d, $J = 14.6$ Hz, 4H), 3.06 (dt, $J = 4.0$, 10.4 Hz, 4H), 2.45 (dsp, $J = 2.3$, 7.0 Hz, 4H), 2.18 (brd, $J = 11.5$ Hz, 4H), 1.60 (brd, $J = 11.0$ Hz, 4H), 1.52 (brd, $J = 9.8$ Hz, 4H), 1.38–1.22 (br, 8H), 1.11–1.05 (brt, $J = 10.8$ Hz, 12H), 0.92 (d, $J = 6.6$ Hz, 12H), 0.90–0.75 (m, 12H), 0.62 (d, $J = 7.1$ Hz, 12H); IR (KBr) 2955, 2925, 2215, 1565, 1455, 1085, 840, 770 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ε) 358 (4.52), 334 (4.62), 314 (4.96), 282 (4.77), 261 (4.87) nm; FABMS (NBA) m/z 1505 [$(M - PF_6)^+$]; Found: C, 61.15; H, 6.24; N, 3.48; F, 13.79; P, 3.70%. Calcd for $C_{84}H_{104}Cu_2F_{12}N_4O_4P_2$: C, 61.12; H, 6.35; N, 3.39; F, 13.81; P, 3.75%.

Copper(I) Complex CL2′: [Cu(L2)](ClO$_4$). To a solution of **CL2** (0.355 g, 0.615 mmol) in acetone (18 mL) was added a solution of tetrabutylammonium perchlorate (1.45 g, 4.39 mmol) in acetone (12 mL) at room temperature. After being stirred at the same temperature for 24 h, the reaction mixture was evaporated to dryness under reduced pressure, and then the resulting residue was washed with AcOEt. Recrystallization of the crude crystals from CH_2Cl_2–hexane gave **CL2′** (0.128 g, 67%) as yellow blocks. mp > 200 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.08 (t, $J = 7.8$ Hz, 2H), 7.85 (d, $J = 7.6$ Hz, 2H), 7.80 (dd, $J = 5.8$, 3.3 Hz, 2H), 7.62 (d, $J = 8.1$ Hz, 2H), 7.59 (dd, $J = 5.7$, 3.3 Hz, 2H), 4.92 (s, 4H), 3.37 (s, 6H); IR (KBr) 2935, 2825, 2210, 1595, 1570, 1490, 1455, 1120, 805, 760, 620 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ε) 358 (4.51), 334 (4.62), 314 (4.95), 282 (4.78), 261 (4.86) nm; FABMS (NBA) m/z 431 [$(M - ClO_4)^+$]; Found: C, 54.03; H, 3.81; N, 5.20; Cl, 6.73%. Calcd for $C_{24}H_{20}ClCuN_2O_6$: C, 54.24; H, 3.79; N, 5.27; Cl, 6.67%. This compound was also prepared directly from **L2** and $Cu(CH_3CN)_4ClO_4$.[20]

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12 All the X-ray diffraction data were collected on a Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation and a rotating anode generator (for **CL2′** and **CL3**) or a Rigaku RAXIS-IV imaging area detector with graphite monochromated Mo Kα radiation (for **CL4**). Calculations were carried out on an SGI Indy using the teXsan[21] crystallographic software package from Molecular Science Corp. The structure was solved by direct methods of SIR92[22] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The refinement of the structure was performed by full-matrix least-squares methods.

13 Crystal data for **CL2′**: [Cu(**L2**)](ClO$_4$): $C_{24}H_{20}ClCuN_2O_6$, $M_r = 531.43$, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.276(2)$, $b = 12.226(2)$, $c = 9.455(1)$ Å, $\alpha = 96.52(1)$, $\beta = 91.81(1)$, $\gamma = 71.93(1)^\circ$, $V = 1121.9(3)$ Å^3, $Z = 2$, $D_{calc} = 1.573$ g cm^{-3}, $T = 223$ K, R (R_w) = 0.029 (0.032) for 4250 reflections with $I > 3.0\sigma(I)$.

14 Crystal data for **CL3**: [Cu(**L3**)](PF$_6$): $C_{34}H_{26}CuF_6N_2O_2P$, $M_r = 701.09$, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.758(1)$, $b = 15.027(1)$, $c = 9.5088(9)$ Å, $\alpha = 96.895(8)$, $\beta = 95.639(9)$, $\gamma = 90.749(8)^\circ$, $V = 1518.2(3)$ Å^3, $Z = 2$, $D_{calc} = 1.534$ g cm^{-3}, $T = 293$ K, R (R_w) = 0.040 (0.040) for 5418 reflections with $I > 3.0\sigma(I)$.

15 Crystal data for **CL4**: [Cu$_2$(**L4**)$_2$](PF$_6$)$_2$: $C_{84}H_{104}Cu_2F_{12}N_4O_4P_2$, $M_r = 1650.79$, triclinic, space group $P1$ (No. 1), $a = 13.707(4)$, $b = 14.891(3)$, $c = 12.030(1)$ Å, $\alpha = 101.65(2)$, $\beta = 115.08(2)$, $\gamma = 97.66(1)^\circ$, $V = 2110.8(2)$ Å^3, $Z = 1$, $D_{calc} = 1.30$ g cm^{-3}, $T = 288$ K, R (R_w) = 0.054 (0.092) for 4679 reflections with $I > 3.0\sigma(I)$.

16 Crystal data for **CL5**: [Cu$_2$(**L5**)$_2$](PF$_6$)$_2$: $C_{84}H_{104}Cu_2F_{12}N_4O_4P_2$, $M_r = 1650.79$, triclinic, space group $P1$ (No. 1), $a = 13.539(4)$, $b = 14.755(2)$, $c = 11.951(2)$ Å, $\alpha = 101.70(1)$, $\beta = 115.11(1)$, $\gamma = 97.44(2)^\circ$, $V = 2053.8(8)$ Å^3, $Z = 1$, $D_{calc} = 1.34$ g cm^{-3}, $T = 198$ K, R (R_w) = 0.052 (0.053) for 5966 reflections with $I > 3.0\sigma(I)$.

17 We were unable to measure ^{1}H NMR spectra of **CL2** at concentration above 20 mM due to the low solubility of **CL2**.

18 We were unable to measure ^{1}H NMR spectra of **CL1** at concentration above 4.2 mM due to the poor solubility of **CL1**.

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