FULL PAPER

A Dicopper(I) Trefoil Knot with *m*-Phenylene Bridges between the Ligand Subunits: Synthesis, Resolution, and Absolute Configuration

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Abstract: A molecular trefoil knot, constructed around two copper(I) centres used as a template, has been synthesized in 29% yield (cyclization step) by the use of 1,3-phenylene spacers between the 1,10-phenanthroline subunits; the double stranded helical precursor complex is formed quantitatively. This latest improvement allowed us to prepare this topologically chiral molecule on a large scale and hence to undertake the resolution of its enantiomers. The resolution technique is based on crystallization of diastereomers with an enantiomerically pure chiral counterion, (*S*)-(+)-1,1'-binaphtyl-2,2'-diyl phosphate [(+)-BNP⁻]. After anion exchange, several tens of milligrams of each enantiomer were isolated, with an excellent enantiomeric excess (*ee* > 98%). The optical purity was determined by ¹H NMR and circular dichroism (CD) spectroscopy. The absolute configuration was established on the basis of an X-ray diffraction study, the dextrorotatory knot corresponding to the left-handed knot. Demetallation with excess KCN yielded the free ligand, which could subsequently be remetallated with silver(I) or copper(I). The chiroptical properties of each species are reported.

Keywords: chiral resolution · copper · molecular topology · template synthesis · trefoil knot

Introduction

Euclidian or *chemical* chirality is the property of rigid molecular objects not to be superimposable to any conformations of their mirror image. This type of chirality is associated with the rigidity of the molecule and with chemically allowed conformational changes.[1–4] The topological properties of a chemical object represent an upper level of description, leading to the notion of *topological* chirality.[5–7] In this manner, contrary to Euclidian enantiomers, two topological enantiomers can not be interconverted by a continuous deformation in a three-dimensional space without breaking a bond. Therefore topological chirality does not imply any rigidity of the architecture.[8, 9] Molecular knots are fascinating objects, not only for their beauty, but also for their chirality. Knots are topologically novel systems *par excellence*, with the simplest of them, that is, the classical trefoil knot, being the archetype of a topologically chiral object (Figure 1).[10–12]

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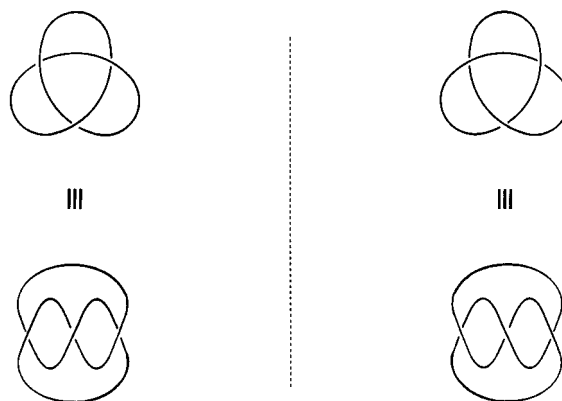a) Left-handed trefoil knot   b) Right-handed trefoil knot

Figure 1. The two topologically equivalent representations of both enantiomers of a trefoil knot.

According to Frisch and Wasserman's definition,[7] structures **a** and **b** are topological enantiomers.

The molecular graph of a topologically chiral molecule is necessarily nonplanar. Made of a single knotted closed ring, a knot can not be represented in a two-dimensional (2D) space without a minimum number of crossing points, three in the case of a trefoil knot. In Figure 2 some of the most well-known prime knots are represented. However, if some knots are chiral, it is noteworthy that others are not, for instance the knot 4_1 represented in Figure 2.
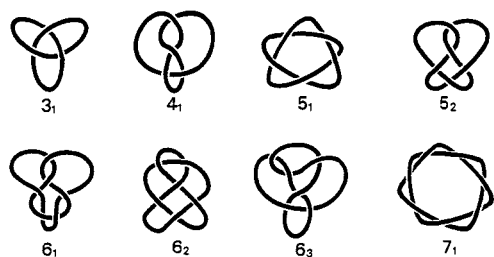
Figure 2. The first eight prime knots.

In 1989, the first trefoil knot was prepared at the molecular level.[13, 14] More recently, two different syntheses have been developed. The first one, introduced by Seeman and co-workers,[15] utilizes synthetic single-stranded DNA fragments that are combined and knotted using enzymes. The second one, developed by Stoddart et al.,[16] is based on the π-donor–π-acceptor gathering effect between aromatic nuclei. We present here the improvements in our strategy, thanks to the optimization of structural parameters, which allowed its preparation on a gram scale[17] and led us to attempt its resolution.[18]

Results and discussion

Synthesis of a racemic trefoil knot: Our strategy for making knots takes advantage of the three-dimensional template effect of transition metals that are able to gather and interlace coordinating molecular strings prior to the ultimate cyclization step. The precursor of a molecular trefoil knot, as shown in Figure 1, is a dinuclear double helix. In the first synthesis,

Abstract in French: *Un nœud de trèfle moléculaire préparé grâce à l'effet de matrice tridimensionnel induit par deux ions cuivre(I) a été obtenu avec un rendement de 29% (étape de cyclisation). Ce progrès a été possible par l'utilisation du pont 1,3-phénylène entre les fragments 1,10-phénanthroline, le précurseur en double hélice se formant alors de manière quantitative. Cette amélioration synthétique a rendu possible la préparation de cette molécule topologiquement chirale a l'échelle du gramme et ainsi à envisager son dédoublement. La méthode de dédoublement que nous avons utilisée est fondée sur la cristallisation de diastéréomères, ceux-ci étant formés par l'utilisation d'un anion optiquement pur, (S)-(+)-1,1'-binaphtyl-2,2'-diyl phosphate ((+)-BNP⁻). Après échange de celui-ci par un anion optiquement inactif, il a été possible d'obtenir plusieurs dizaines de milligrammes de chaque énantiomère, ceci avec un excellent excès énantiomérique (ee > 98%). La pureté optique a été déterminée par RMN-¹H et par dichroïsme circulaire. La configuration absolue a également été déterminée sur la base d'une étude par diffraction des rayons X, le nœud dextrogyre correspondant au nœud gauche. La démétallation avec un excès de KCN nous permet d'obtenir le ligand libre qui a été remétallé avec de l'argent(I) ou du cuivre(I). Les propriétés optiques de chaques espèces sont rapportées.*

the modest yield was due to the simultaneous formation of a face-to-face complex (major species), in equilibrium with the double helix.[19] A 1,3-phenylene spacer, already used with success by others in the construction of helical complexes,[20–22] appeared very appealing to bridge the two phenanthroline fragments in the precursor ligand.

Synthesis of a bisphenanthroline with a 1,3-phenylene bridge: Bisphenanthroline **1** was obtained after reaction at room temperature of 2-(*p*-anisyl)-1,10-phenanthroline[23] with half an equivalent of 1,3-dilithiobenzene formed by interconversion of 1,3-dibromobenzene with *tert*-butyllithium.[24] After hydrolysis of the reaction mixture at 0°C, followed by rearomatization with excess manganese dioxide, chromatography on alumina afforded pure **1** in a 66% yield. The methylic ethers were deprotected in refluxing pyridinium chloride, according to a method described by Curphey et al.[25] Despite the hard reaction conditions, diphenol **2** was obtained in a 94% yield after neutralization with 0.1M NaOH and drying under vacuum in the presence of phosphorus pentoxide.

Preparation of a copper(I) double helix with a labile anion: To introduce the chiral auxiliary necessary in the resolution step, a labile anion, unlike the classical BF_4^- or PF_6^- which can not easily be exchanged, is required. Therefore, we performed the metallation of **1** with a copper salt bearing a labile, non-coordinating counterion. Triflate, which is known for these properties,[26] seemed particularly well-suited. Copper(I) triflate can be easily generated in situ by reaction of copper(II) triflate in the presence of a reducing agent. Copper(II) triflate was prepared following Jenkins' method,[27] by addition of triflic acid onto a solution of copper(II) carbonate in acetonitrile. After recrystallization, this salt was obtained in 85% yield.

One equivalent of copper(II) triflate was then added at room temperature to the bischelating diphenolic strand **2** in the presence of a reductant (ascorbic acid or hydrazine). Mass spectroscopy confirmed that the dark-red complex, obtained quantitatively, contained two copper ions and two ligands, and ¹H NMR showed that the molecule had a high degree of symmetry. The four phenanthrolines, the four anisyls and the two 1,3-phenylene bridges are magnetically equivalent; this is a characteristic feature of a double helix that possesses three C_2 symmetry axes.[2, 3, 13]

In addition, this ¹H NMR spectrum shows striking differences compared with that of the free ligand. Protons H_o are significantly shielded (from 8.45 to 7.10 ppm), as well as H_m (from 6.93 to 5.75 ppm) and especially H_3 (from 8.63 to 6.57). All these protons are located in the shielding cones of the phenanthroline fragments of the double helix. A crystallographic study finally confirmed the double-helical structure.[17]

A double helix is a classically (but not topologically) chiral object. The coordination of the first copper(I) ion determines the rotation direction of the helix and therefore its stereochemistry. It can either turn right (P double helix) or left (M double helix). This chirality, purely of Euclidian nature, is responsible for the topological chirality of the copper(I) knot.

Preparation of a copper(ı) knot: The crystallographic study of the double helix also showed that, owing to an important twisting, the terminal phenolic functionalities are well-oriented to favour the double cyclization leading to the knot. The intermolecular reactions leading to oligomers are disfavoured by the use of pseudo-high-dilution reaction conditions: a suspension of cesium carbonate is progressively added to a DMF solution containing in a 1:1 ratio the diiodo derivative of hexaethyleneglycol[28] and the double helix (initial concentration of ∼5 mmol L⁻¹). The reactive species (phenolate) is therefore generated in very low concentration, which favours intramolecular reactions and prevents the copper(ı) complex from being in a strongly basic medium, in which it is unstable. After a reaction time of forty hours and performance of chromatography twice in succession over silica, the triflate of the copper(ı) knot was isolated in a 29% yield; this is very satisfying given that the cyclization involves the connection of eight reaction centres.

The ^{1}H NMR spectrum of $4^{2+} \cdot 2\,TfO^-$ is very similar to that of the double helix, except the appearance of a broad multiplet (between 4.20 and 3.20 ppm) corresponding to the signals expected for the 48 protons of the two hexaethyleneglycol chains. The mass spectrum shows a large molecular ion peak at the expected value ($m/z = 2003.0$ $[M - TfO]^+$). However, the knotted structure could only be strictly evidenced by a 2D ROESY NMR experiment, which showed interfragment NOE interactions between protons 5 and 6 of the phenanthroline subunits (Figure 3) and the central protons of the polyoxyethylenic chains. Moreover, a crystallographic study confirmed the knotted structure of this complex (vide infra).

Resolution: The resolution step of a chiral molecule is sometimes difficult but always crucial.[29, 30] Topologically chiral [2]-catenanes have been described,[31] but their resolution could only be carried out at the analytical level.[32] The strategy used here to prepare knots implies that the target molecules be obtained as cationic dicopper(ı) complexes. Therefore we considered the possibility of interconverting both enantiomers into a pair of diastereomeric salts by combining them with an optically active anion. Binaphthyl phosphate (BNP⁻)[33] drew our attention because its chirality arises from the binaphthyl core, which is twisted. This helical structure is reminiscent of that of the copper(ı) double helix, precursor of the knot. Besides, both compounds are aromatic and therefore, we could expect some potentially helpful stacking interactions.[34]

These structural similarities should enable strong interactions between the two moieties, possibly leading to a marked differentiation of the properties
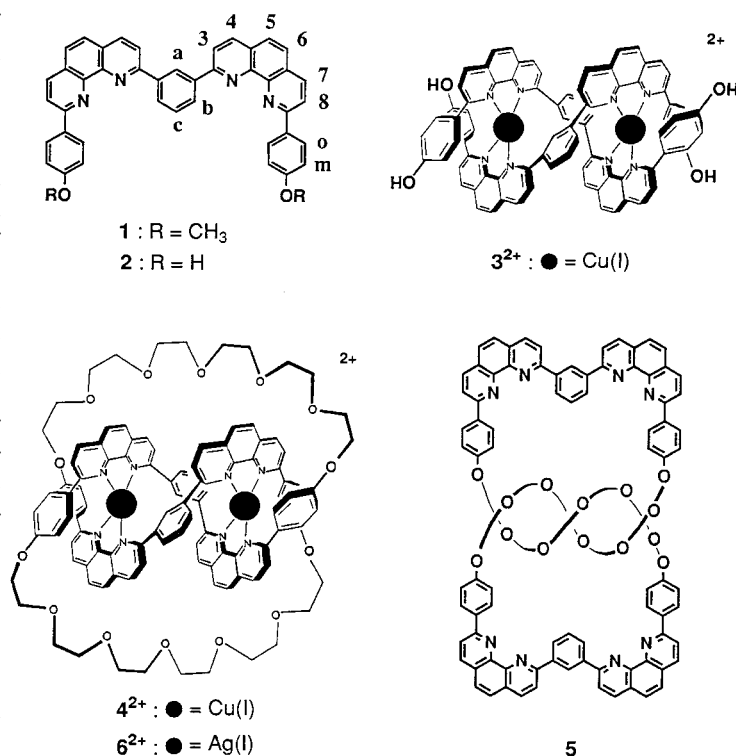

Figure 3. Synthetic strategy and chemical structure of the organic precursors and of the knots.

of both diastereomers (e.g., their solubility), making their resolution possible by selective crystallization. The principle of the resolution process is represented in Figure 4.

The racemic mixture of the knot was converted into diastereomers by means of a liquid–liquid extraction; this takes advantage of the solubility of sodium triflate in water compared with the insolubility of binaphthylphosphate salts. Sodium binaphthylphosphate and the copper(ı) knot triflate were dissolved in dichloromethane. Sodium triflate was progressively extracted by a water flow running through the medium. The anion exchange was monitored by TLC (SiO₂; eluent: CH₂Cl₂/10% MeOH), the counterion having a strong
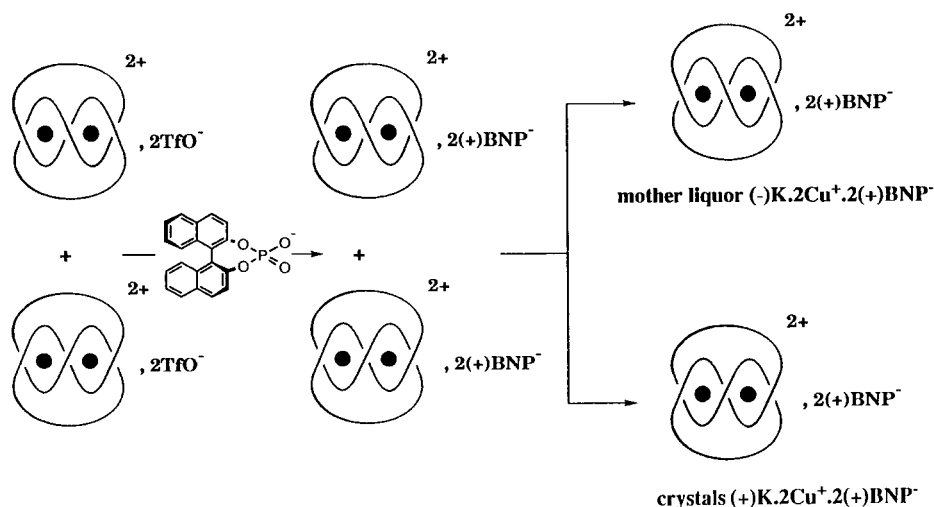

Figure 4. Principle of the resolution of the dicopper(ı) molecular trefoil knot 4^{2+}. The chiral auxiliary used is (S)-(+)-1,1'-binaphthyl-2,2'-diyl phosphate (BNP⁻).

influence on the polarity of the complex (the difference in R_f is 0.2). After 48 hours at room temperature, the exchange was complete.

The ^{1}H NMR spectrum of the diastereomeric mixture appeared to be very striking. Each signal was split into two, which clearly indicated a strong difference in association between the chiral auxiliary and each enantiomer of the knot. This difference was large enough to confer the two diastereomers different solubilities. Indeed we could crystallize (+)-4^{2+}·2(+)-BNP$^-$ in a mixture of nitromethane and benzene,[18] whereas the levorotatory knot remained in the mother liquor.

Typically, 100 mg of (±)-4^{2+}·2(+)-BNP$^-$ were dissolved in 5 mL of nitromethane and this solution was placed in a crystallization tube. Benzene (nonsolvent) was carefully added on top, thereby provoking, by slow diffusion into the nitromethane solution, the crystallization of dark-red needles. After filtration of these needles, the mother liquor was evaporated to dryness. By measuring the rotatory power of both samples and by recording their ^{1}H NMR spectra, we could determine that the mother liquor contained 33.5 mg of optically pure (−)-4^{2+}·2(+)-BNP$^-$ (diastereomeric excess >98%) and that the 66.3 mg of crystals contained 70% of (+)-4^{2+}·2(+)-BNP$^-$, that is, a 40% diastereomeric excess (more details are given in the Experimental Section).

A second crystallization by diffusion of benzene vapours in a nitromethane solution of these crystals yielded 44.1 mg of optically pure dextrorotatory diastereomer (+)-4^{2+}·2(+)-BNP$^-$.

The ^{1}H NMR spectra (selection of the most interesting aromatic signals) of each isolated diastereomer and of their initial mixture are shown in Figure 5. Chemical shifts of the most representative protons are given in Table 1.

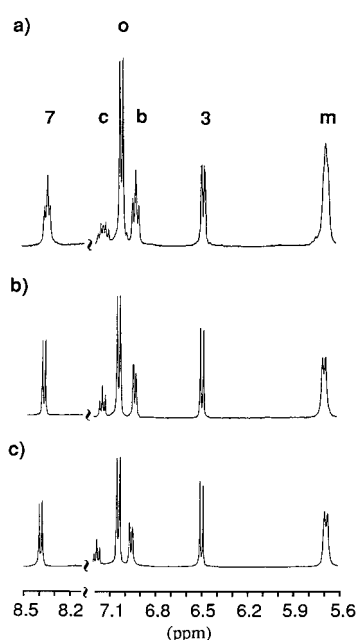The difference in chemical shift from one diastereomer to the other may give some indication as to the location of the

Table 1. ^{1}H NMR (400 MHz) chemical shifts of a selection of aromatic protons for the two diastereomers (−)-4^{2+}·2(+)-BNP$^-$ and (+)-4^{2+}·2(+)-BNP$^-$.

	H_a	H_7	H_c	H_o	H_b	H_3	H_m
(−)-4^{2+}·2(+)-BNP$^-$	9.697	8.394	7.181	7.037	6.951	6.482	5.665
(+)-4^{2+}·2(+)-BNP$^-$	9.680	8.367	7.133	7.023	6.916	6.468	5.665
$\Delta\delta$ [ppm]	0.017	0.027	0.048	0.014	0.035	0.014	0

BNP$^-$ anions. Differences appear large for the protons on the *m*-phenylene spacer ($\Delta\delta = 0.035$ and 0.048 for H_b and H_c, respectively) but weak for the peripheral ones ($\Delta\delta = 0.014$ and 0.000 for H_o and H_m, respectively). These observed chemical shifts arise most probably from a preferential interaction of the (+)-BNP$^-$ anion with the central core of the double helix.

Optical properties: The molar rotation of each diastereomer has been measured in dichloromethane. The experimental values are not exactly opposite due to the contribution of the (+)-BNP$^-$ anion (see Experimental Section for more details). In order to isolate the pure enantiomers, (+)BNP$^-$ was exchanged for PF$_6^-$ by addition of a large excess of potassium hexafluorophosphate. Now, the molar rotations obtained for each enantiomer are perfectly equal and opposit in sign. The circular dichroism (CD) spectra of each enantiomer are presented in Figure 6; they are mirror images over the whole region of the spectrum. In the visible, $\Delta\varepsilon$ reaches an extremum (+ or − 20.7 mol^{-1}L cm^{-1}) that corresponds to the absorption maximum of the metal-to-ligand charge-transfer (MLCT) transition at 510 nm.

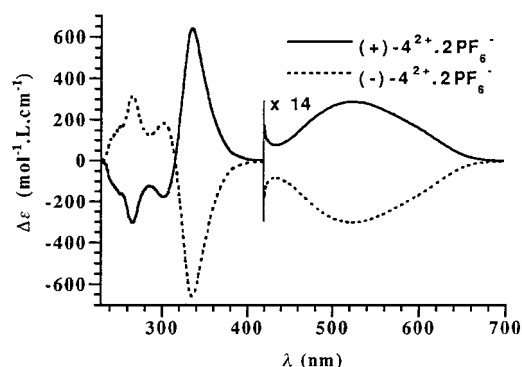Figure 6. Circular dichroism spectra of both enantiomers of the dicopper(I) trefoil knot (−)-4^{2+}·2 PF$_6^-$ (dotted line) and (+)-4^{2+}·2 PF$_6^-$ (plain line) in CH$_2$Cl$_2$; these are perfect mirror images.

To finally accede to metal-free, purely topologically chiral molecules, both enantiomers were demetallated separately by refluxing them in acetonitrile in the presence of an excess of potassium cyanide leading to the free knots (+)-**5** and (−)-**5**. Both were pale-yellow glassy compounds and their molar rotation was determined. A value of + or − 20000 was found, which is high and comparable with those reported for some helicenes.[35–37] As expected, owing to the very different hypothetical electronic spectra of both species, this value strongly contrasts with the very low theoretical value calculated by Frisch and Wasserman for a knot made of 66 CH$_2$

Figure 5. ^{1}H NMR at 400 MHz in CD$_2$Cl$_2$ (aromatic region, selected peaks) of a) the racemate, b) diastereomer (+)-4^{2+}·2(+)-BNP$^-$ and c) diastereomer (−)-4^{2+}·2(+)-BNP$^-$.

units.[38] The high rotatory power found in our case is probably related to the large dissymmetry in the organic skeleton of knots (+)- or (−)-$4^{2+}\cdot 2\,PF_6^-$ (flexible polyoxyethylenic fragments alternating with rigid aromatic subunits).

Moreover, the chromophore also contributes greatly. From Drude's equation:[30] $\alpha = K/(\lambda - \lambda_o)$, in which α is the rotatory power measured at wavelength λ, λ_o the wavelength of the closest absorption maximum and K a constant characteristic of a molecule, one can see that the closer the wavelength used for the measurment of α is to an absorption maximum, the higher the rotatory power. In our case, λ corresponds to the D ray of sodium (589 nm), so it is much closer to the absorption maximum of the n−π* transition of the phenanthroline groups ($\lambda_o \sim 310$ nm) than to that of the σ−σ* transition of the methylenic groups ($\lambda_o < 200$ nm) considered by Frisch and Wasserman. Therefore a smaller rotatory power is expected in the $(CH_2)_{66}$ case.

Remetallation of the free knotted ligand could be achieved either with copper(ɪ) or with silver(ɪ). The $4^{2+}\cdot 2\,PF_6^-$ complex regenerated with copper(ɪ) displayed, as expected, an identical rotatory power compared with that of the original $4^{2+}\cdot 2\,PF_6^-$, whereas a really different optical rotatory power is found for the knot $6^{2+}\cdot 2\,BF_4^-$ remetallated with silver(ɪ) (see Experimental Section for more details). This is in agreement with the Drude equation,[30] since the silver(ɪ) knot does not absorb in the visible region. Their CD spectra are also strongly different from those observed for the copper(ɪ) complexes (Figure 7). The BF_4^- counterion being optically inactive, they are perfect mirror images over the entire domain. $\Delta\varepsilon$ reaches an extremum, + or − 750 mol⁻¹ L cm⁻¹, which corresponds to a π−π* transition at 336 nm.
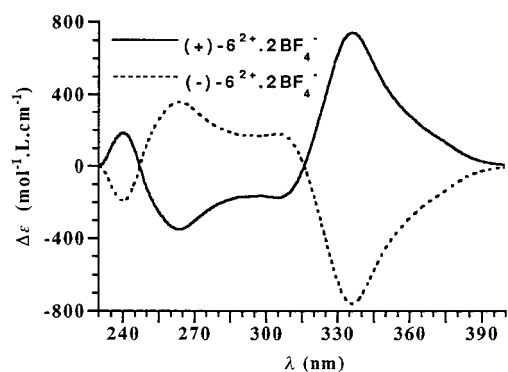

Figure 7. Circular dichroism spectra of both enantiomers of the disilver(ɪ) trefoil knot (−)-$6^{2+}\cdot 2\,BF_4^-$ (dotted line) and (+)-$6^{2+}\cdot 2\,BF_4^-$ (plain line) in CH_2Cl_2.

Radiocrystallographic study and absolute configuration: Crystals suitable for X-ray analysis were obtained by dissolution of 60 mg of the dextrorotatory dicopper(ɪ) knot (+)-$4^{2+}\cdot 2\,PF_6^-$ in 2-nitropropane and liquid diffusion of benzene. The absolute configuration of the dextrorotatory resolved knot has been determined. The X-ray crystallographically determined molecular structure is presented Figure 8.[39]

The molecule has effective D_2 symmetry, with three mutually perpendicular pseudo-twofold axes, one joining the two copper cations, one passing through the middle of the two bridges, and the third one being perpendicular to the others,
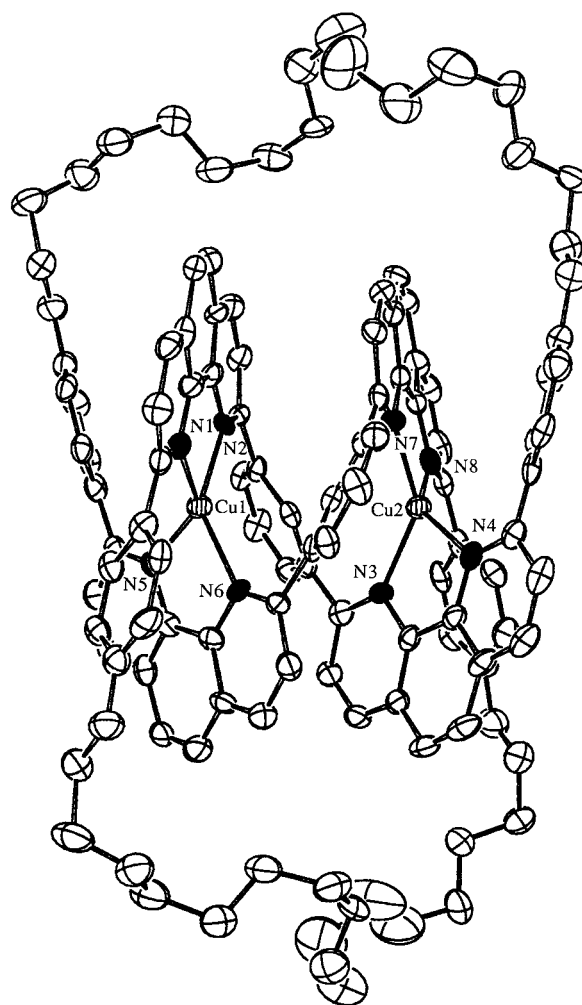

Figure 8. Crystal structure of the dextrorotatory dicopper(ɪ) trefoil knot (+)-$4^{2+}\cdot 2\,PF_6^-$. ORTEP representation showing the numbering scheme adopted for copper and nitrogen atoms (for the sake of clarity, please note the numbering of the nitrogen atoms is different from the original one reported to Cambridge Crystallographic Data Centre). The solvent molecules, PF_6 anions and hydrogen atoms have been omitted and the nitrogen atoms are shown in black.

passing through the central oxygens of the two polyoxyethylene chains. Selected bond distances and angles are given in Table 2.

The tight molecular structure of 4^{2+} is characterized by a very short Cu−Cu distance (4.76 Å), whereas the coordination

Table 2. Bond distances and angles of the two pseudo-tetrahedral copper centers in the complex (+)-$4^{2+}\cdot 2\,PF_6^-$.

Cu1 environment		Cu2 environment	
Bond distances [Å]			
Cu1−N1	2.057	Cu2−N3	2.067
Cu1−N2	2.066	Cu2−N4	2.063
Cu1−N5	2.057	Cu2−N7	2.067
Cu1−N6	2.066	Cu2−N8	2.064
Angles [°]			
N1-Cu1-N2	82.14	N3-Cu2-N4	80.94
N1-Cu1-N5	138.05	N3-Cu2-N7	140.16
N1-Cu1-N6	112.14	N3-Cu2-N8	113.14
N2-Cu1-N5	112.14	N4-Cu2-N7	113.14
N2-Cu1-N6	141.16	N4-Cu2-N8	139.86
N5-Cu1-N6	82.14	N7-Cu2-N8	80.94

polyhedra around each metal appear as strongly distorted tetrahedra, the two centers having very similar coordination angles as shown in Table 2. The chelate bite of the phenanthroline ligand imposes two N-Cu-N angle values of 80 to 82°, but the other N-Cu-N angles vary from 112 to 141°. Each copper atom is bound to two phenanthrolines through four nitrogen atoms. The Cu−N distances range from 2.05 to 2.07 Å; they are close to the values found in other copper(I) complexes of related ligands.[14, 17, 40]

Finally, it was possible to determine the absolute configuration of $(+)$-$4^{2+} \cdot 2\,PF_6^-$. It was found that the crystals of the dextrorotatory knot correspond to the Λ knot, that is, the enantiomer containing a double helix of absolute configuration M.

Conclusion

Selective crystallization allowed us to resolve a dicopper(I) trefoil knot. To our knowledge, it is the first preparative resolution of topological enantiomers. The absolute configuration has been determined by X-ray crystallography. Topologically chiral molecules are those whose enantiomers can not be interconverted by continuous deformation, therefore racemization is excluded as long as no bond in their organic backbone is broken. The combination of this latter topological property with the high thermodynamic stability of copper(I) 2,9-diphenylphenanthroline complexes provides us with potential reagents and catalysts for various enantioselective processes.

Experimental Section

General procedures: The following chemicals were obtained commercially and were used without further purification: Cs_2CO_3 (Aldrich), KCN (Janssen), KPF_6 (Janssen). Some materials were prepared according to literature procedures: 2-(p-anisyl)-1,10-phenanthroline,[23] copper(II) triflate,[27] hexaethyleneglycol diiodide,[28] (S)-(+)-1,1'-binaphthyl-2,2'-phosphoric acid,[33] and $Cu(MeCN)_4PF_6$.[41] Dry solvents were obtained by distillation over suitable dessicants (Et_2O and THF from Na/benzophenone, CH_2Cl_2 from P_2O_5, pyridine from potassium hydroxide). The other anhydrous solvents were of commercial analytical grade: acetonitrile, dimethylformamide, methanol, absolute ethanol, toluene, nitromethane. Thin-layer chromatography (TLC) was performed on aluminium sheets coated with silica gel 60 F_{254} (Merck 5554), or coated with neutral alumina 60 F_{254} (Merck 5550). After elution, the plates were either scrutinized under a UV lamp or exposed to I_2. Column chromatography was carried out on silica gel 60 (Merck 9385, 230–400 mesh) or neutral alumina 90 (Merck 1076, 0.060–0.200 mm). UV/Vis spectra were recorded on a Kontron Instruments UVIKON 860 spectrophotometer. Fast atom bombardment mass spectrometry (FABMS), were recorded in the positive-ion mode with either a krypton primary-atom beam in conjunction with a 3-nitrobenzyl alcohol matrix and a Kratos MS80RF mass spectrometer coupled to a DS90 system, or a xenon primary-atom beam with the same matrix and a ZAB-HF mass spectrometer. Electrospray mass spectrometry (ES-MS) were recorded in the positive-ion mode with VG-BIOQ triple quadripole. The ^1H NMR spectra were recorded on either Bruker WP200SY (200 MHz) or AM400 (400 MHz) spectrometers. The melting points were measured on a Bioblock IA 8103 apparatus or on a Büchi SMP-20 apparatus and are not corrected. Circular dichroism (CD) measurements were performed in CH_2Cl_2 with a Jobin Yvon CD6 spectrophotometer. Cyclic voltammetry (CV) was realized with a Pt working electrode, a Pt control electrode and a saturated calomel electrode as reference. Potentiostat EG&G Princeton Applied Research model 273A. $(nBu)_4NPF_6$ 0.1M was used as support electrolyte.

Preparation of bisphenanthroline 1: A solution of tert-butyllithium (12 mL, 16 mmol, 1.34 M) was added dropwise and under argon to a degassed solution of m-dibromobenzene (0.94 g, 4 mmol) in freshly distilled THF (50 mL) maintained at −78 °C. The reaction mixture was stirred at −78 °C for 1 hour; the temperature was then brought up to +10 °C and immediately back down to −78 °C for an additionnal hour. It was then added through a cannula to a suspension of 2-(p-anisyl)-1,10-phenanthroline (2.3 g, 8 mmol) in anhydrous THF (150 mL). The purple solution thus obtained was stirred for 50 hours under argon and at room temperature and then hydrolyzed at 0 °C by adding water (150 mL). A red solid started to precipitate. The THF was evaporated and the reaction mixture was taken up in CH_2Cl_2/H_2O (1:1). The organic layer was decanted and the aqueous layer was extracted with CH_2Cl_2 (3 × 200 mL). The combined organic layers were rearomatized by treatment with MnO_2 (20 g, excess), dried over $MgSO_4$ and filtered and the filtrate was evaporated to dryness. Chromatography on alumina (eluent: $CHCl_3/0$–10 % MeOH) afforded 1 in a 66 % yield (1.69 g, 2.9 mmol) as a colourless solid. M.p. 244 °C; MS (FAB$^+$): m/z: 647.2 ([M+H]$^+$, calcd 647.2; 100 %), 324.1 ([M+2H]$^{2+}$, calcd 324.1; 33 %); ^1H NMR ([D_6]DMSO, 200 MHz): δ = 9.93 (t, ^4J = 1.5 Hz, 1 H; H_a), 8.71 (d, ^3J = 8.5 Hz, 2 H; H_4), 8.67 (dd, ^3J = 7.7 Hz, ^4J = 1.5 Hz, 1 H; H_b), 8.63 (d, ^3J = 8.5 Hz, 2 H; H_3), 8.54 (d, ^3J = 8.5 Hz, 2 H; H_7), 8.44 (d, ^3J = 8.8 Hz, 4 H; H_o), 8.28 (d, ^3J = 8.5 Hz, 2 H; H_8), 8.05 (s, 4 H; H_{5-6}), 7.90 (t, ^3J = 7.7 Hz, 1 H; H_c), 3.90 (s, 6 H; OMe); $C_{44}H_{30}N_4O_2$ (646.74): calcd C 81.71, H 4.68, N 8.66; found C 81.49, H 4.86, N 8.54.

Preparation of diphenol 2: Hydrochloric acid (17.6 mL, 12 M) was added to analytical grade pyridine (16 mL) under rapid mechanical stirring. The flask was equipped for distillation and water was distilled from the mixture until its internal temperature rose to 210 °C. Once the anhydrous pyridinium chloride solution had been cooled down to 150 °C, 1 (1.14 g, 1.8 mmol) was added at once as a solid and under an argon flush. The mixture was then refluxed (210 °C) under argon for 3 hours. After hydrolysis by hot water (60 mL), filtration onto filter paper gave 1.8 g of a yellow solid. This solid was suspended in MeOH/H_2O (3:1, 140 mL) and neutralized with a 0.1M NaOH solution. The resulting orange suspension was filtered off and dried for 36 hours under high vacuum in the presence of P_2O_5 to yield 1.10 g of pure 2 (1.7 mmol, 94 % yield) as an orange solid. ^1H NMR ([D_6]DMSO, 200 MHz): δ = 9.77 (s, 1 H; H_a), 8.76 (d, ^3J = 7.9 Hz, 2 H; H_b), 8.71 (d, ^3J = 8.5 Hz, 2 H; H_4), 8.63 (d, ^3J = 8.5 Hz, 2 H; H_3), 8.53 (d, ^3J = 8.5 Hz, 2 H; H_7), 8.45 (d, ^3J = 8.5 Hz, 4 H; H_o), 8.31 (d, ^3J = 8.5 Hz, 2 H; H_8), 8.03 (s, 4 H; H_{5-6}), 7.95 (t, ^3J = 7.9 Hz, 1 H; H_c), 6.93 (d, ^3J = 8.5 Hz, 4 H; H_m); $C_{42}H_{26}N_4O_2$ (618.69): calcd C 81.54, H 4.24, N 9.06; found C 81.05, H 4.71, N 8.74; m.p. 252 °C (decomp); MS (FAB$^+$): m/z: 619.1 ([M+H]$^+$, calcd 619.2; 100 %), 310 ([M+2H]$^{2+}$, calcd 310.1; 6 %)

Preparation of the dicopper(I) double helix $3^{2+} \cdot 2\,TfO^-$: A degassed solution of copper(II) triflate (621 mg, 1.72 mmol) in acetonitrile (20 mL) was added under argon to a suspension of 2 (900 mg, 1.45 mmol) and ascorbic acid (302 mg, 1.72 mmol) in DMF (100 mL) at room temperature. The resulting dark-red mixture was stirred for one hour under argon. The solvent was evaporated and the residue washed with water and dried under vacuum. Pure 3 was obtained in a quantitative yield (1.22 g, 0.72 mmol) as a dark-red solid. ^1H NMR ([D_6]DMSO, 200 MHz): δ = 9.55 (br s, 2 H; H_a), 8.60 (d, ^3J = 8.5 Hz, 4 H; H_7), 8.04 (AB, ^3J = 8.9 Hz, 8 H; H_{5-6}), 7.93 (d, ^3J = 8.4 Hz, 4 H; H_4), 7.82 (d, ^3J = 8.5 Hz, 4 H; H_8), 7.16 (t, ^3J = 8.9 Hz, 2 H; H_c), 7.10 (d, ^3J = 8.7 Hz, 8 H; H_o), 7.04 (d, ^3J = 8.9 Hz, 4 H; H_b), 6.57 (d, ^3J = 8.4 Hz, 4 H; H_3), 5.75 (d, ^3J = 8.7 Hz, 8 H; H_m); m.p. 238 °C (decomp); cyclic voltammetry (CV): two reversible distinct waves for Cu^{II}–Cu^I with E° ($3^{3+}/3^{2+}$) and ($3^{4+}/3^{3+}$) = +0.69 and +0.91 V vs. SCE in MeCN; MS (ES$^+$): m/z 1566.7 ([M − TfO]$^+$, calcd 1567.3; 12 %), 709.2 ([M − 2 TfO]$^{2+}$, calcd 709.2; 100 %); UV/Vis(CH_2Cl_2): λ_{max} (ε) = 233 (128700), 252 (118800), 326 (76300), 427 (sh, 3900), 518 nm (3300).

Preparation of the dicopper(I) double helix $3^{2+} \cdot 2\,BF_4^-$ or $3^{2+} \cdot 2\,PF_6^-$: A degassed solution of copper(I)tetrakisacetonitrile BF_4^- or PF_6^- salt in acetonitrile (20 mL) was added under argon to a suspension of one equivalent of 2 in DMF (100 mL) at room temperature. The resulting dark-red mixture was stirred for one hour under argon. The solvent was evaporated and the residue was washed with water and dried under vacuum. Pure 3 was obtained in a quantitative yield as a dark-red solid. The ^1H NMR and UV/Vis spectra are analogous to the spectra obtained with the triflate salt.

Preparation of the dicopper(I) knot $4^{2+} \cdot 2\,TfO^-$: Small fractions of a suspension of Cs_2CO_3 in DMF (932 mg overall, 2.86 mmol) were added through cannula to a solution of $3^{2+} \cdot 2\,TfO^-$ (1.18 g, 0.70 mmol) and hexaethyleneglycol diiodide (790 mg, 1.57 mmol) in DMF (300 mL) at $60\,^\circ$C under argon. The colour of the mixture progressively changed from yellow to dark red. The reaction was followed by TLC on silica plates (eluent: $CH_2Cl_2/MeOH$ 90:10) and showed the disappearance of the chain, which was compensated for by a further addition of this reactant (466 mg, 0.93 mmol) during the reaction. The reaction mixture was stirred at $60\,^\circ$C under argon for a further 24 hours. The DMF was then evaporated under high vacuum ($50\,^\circ$C) and the dark-red residue dissolved in CH_2Cl_2/H_2O (1:1). The organic layer was decanted, insoluble oligomers were eliminated and the aqueous layer was extracted three times with CH_2Cl_2. The organic layers were combined and the solvent was evaporated. The residue was treated by a copper(II) triflate solution (8 g, excess) in CH_3CN (300 mL) at room temperature and was stirred for 24 hours. This was done in order to have TfO^- as the only counter-anion (the reaction mixture also contains I^- and CO_3^{2-} anions). After evaporation of the solvent, the residue was dissolved in CH_2Cl_2 and washed 3 times with water. After decantation, the organic phase was dried over $MgSO_4$ and filtered. The filtrate was evaporated to dryness and crude $4^{2+} \cdot 2\,TfO^-$ was chromatographed on silica (eluent: $CH_2Cl_2/0-12\%MeOH$) to yield 431 mg of pure $4^{2+} \cdot 2\,TfO^-$ (0.20 mmol, 29% yield) as a dark-red solid. ^1H NMR (CD_2Cl_2, 200 MHz): $\delta = 9.72$ (br s, 2H; H_a), 8.42 (d, $^3J = 8.4$ Hz, 4H; H_7), 7.98 (AB, $^3J = 8.8$ Hz, 8H; H_{5-6}), 7.96 (d, $^3J = 8.4$ Hz, 4H; H_4), 7.66 (d, $^3J = 8.4$ Hz, 4H; H_8), 7.23 (t, $^3J = 7.8$ Hz, 2H; H_c), 7.07 (d, $^3J = 8.6$ Hz, 8H; H_o), 6.98 (dd, $^3J = 7.8$ Hz, $^4J = 1.2$ Hz, 4H; H_b), 6.56 (d, $^3J = 8.4$ Hz, 4H; H_3), 5.70 (d, $^3J = 8.6$ Hz, 8H; H_m), 4.20–3.20 (m, 48H; CH_2). The latter assignment was confirmed by 2D NMR spectroscopy (ROESY). M.p. $>280\,^\circ$C; MS (FAB$^+$): m/z: 2003.0 ($[M - TfO]^+$, calcd 2003.5; 14%), 1853.9 ($[M - 2\,TfO + e^-]^+$, calcd 1854.6; 13%), 927.2 ($[M - 2\,TfO^-]^{2+}$, calcd 927.3; 13%); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 237 (118100), 253 (115000), 324 (69200), 425 (sh, 3700), 520 nm (2960); $C_{110}H_{96}Cu_2F_6N_8O_{20}S_2$ (2155.22): calcd C 61.30, H 4.49, N 5.20; found C 61.08, H 4.37, N 5.07. The same procedure can be applied to obtain the dicopper(I) trefoil knot with BF_4^- or PF_6^- counter-anion starting with the corresponding double-helix. For the complex with the BF_4^- anion, the cyclic voltammogram was measured (CV) showing two reversible distinct waves for $Cu^{II}-Cu^{I}$ with E^o ($3^{3+}/3^{2+}$) and ($3^{4+}/3^{3+}$) = $+0.68$ and $+0.92$ V vs. SCE, respectively, in MeCN.

Preparation of the diastereomers of the knot: An aqueous solution of NaOH (3.3 mL, 0.33 mmol, 0.1 M) was added to a suspension of binaphthylphosphoric acid (115 mg, 0.33 mmol) in CH_3CN (50 mL). The solvent was evaporated and the residue dissolved in CH_2Cl_2 (150 mL). $(\pm)$-$4^{2+} \cdot 2\,TfO^-$ (320 mg, 0.15 mmol) was then added; it immediately dissolved in the mixture. Liquid–liquid extraction was performed at room temperature over 24 hours in order to replace TfO^- by binaphtylphosphate (BNP^-). The ion exchange was followed by TLC on alumina plates (eluent: $CH_2Cl_2/5\%$ MeOH). The organic layer was then decanted and dried over $MgSO_4$. After filtration, the solvent was evaporated to give $(\pm)$-$4^{2+} \cdot 2(+)$-BNP^- as a red solid (380 mg, 0.15 mmol, quantitative yield). ^1H NMR showed that each signal of the Cu^I knot was split into two, which confirmed the presence of two diastereomers and showed the presence of the BNP^- anion.

Resolution of $(-)$-$4^{2+} \cdot 2(+)$-BNP^- and $(+)$-$4^{2+} \cdot 2(+)$-BNP^-: A saturated solution of the diastereomers (510 mg, 0.2 mmol) in a 1:1 mixture of dichloromethane and benzene was placed in a crystallization tube (internal diameter 1 cm, length 20 cm). Some benzene was then added precautiously, so that the surface of the red solution of knot was not damaged. After two weeks diffusion, the needles obtained were filtered off and the mother liquor was evaporated. From their ^1H NMR spectra and their rotatory powers, it was established that the crystals (207 mg) were diastereomerically pure and that the mother liquor (303 mg) had been strongly enriched into the other diastereomer (68% diastereomeric excess). This sample was crystallized a second time, with the use of a crystallization tube of 0.7 cm internal diameter and of 20 cm length. After diffusion of benzene, the needles obtained were filtered off and the mother liquor was evaporated. From their ^1H NMR spectra and their rotatory powers, it was established that the mother liquor (57 mg) was diastereomerically pure and that the crystals (246 mg) were not (60% diastereomeric excess).

$(-)$-$4^{2+} \cdot 2(+)$-BNP^-: $[M]_D = -66000$ ($c = 5.25 \times 10^{-6}$ in CH_2Cl_2); CD (CH_2Cl_2): λ_{max} ($\Delta\varepsilon$) = 264 ($+337$), 298 ($+176$), 333 (-631), 510 nm (-21.3); ^1H NMR (CD_2Cl_2, 200 MHz): $\delta = 9.70$ (br s, 2H; H_a), 8.39 (d,

$^3J = 8.4$ Hz, 4H; H_7), 7.9–8.0 (m, 20H; $H_{4-5-6-BNP}$), 7.2–7.8 (m, 20H; H_{8-BNP}), 7.18 (t, $^3J = 7.8$ Hz, 2H; H_c), 7.04 (d, $^3J = 8.6$ Hz, 8H; H_o), 6.95 (dd, $^3J = 7.8$ Hz, $^4J = 1.2$ Hz, 4H; H_b), 6.48 (d, $^3J = 8.4$ Hz, 4H; H_3), 5.67 (d, $^3J = 8.6$ Hz, 8H; H_m), 4.20–3.20 (m, 48H; CH_2).

$(+)$-$4^{2+} \cdot 2(+)$-BNP^-: $[M]_D = +73000$ ($c = 4.57 \times 10^{-6}$ in CH_2Cl_2); CD (CH_2Cl_2): λ_{max} ($\Delta\varepsilon$) = 265 (-203), 299 (-179), 333 ($+586$), 508 nm ($+20.7$); ^1H NMR (CD_2Cl_2, 200 MHz): 9.68 (br s, 2H; H_a), 8.37 (d, $^3J = 8.4$ Hz, 4H; H_7), 7.9–8.0 (m, 20H; $H_{4-5-6-BNP}$), 7.2–7.8 (m, 20H; H_{8-BNP}), 7.13 (t, $^3J = 7.8$ Hz, 2H; H_c), 7.02 (d, $^3J = 8.6$ Hz, 8H; H_o), 6.92 (dd, $^3J = 7.8$ Hz, $^4J = 1.2$ Hz, 4H; H_b), 6.47 (d, $^3J = 8.4$ Hz, 4H; H_3), 5.67 (d, $^3J = 8.6$ Hz, 8H; H_m), 4.20–3.20 (m, 48H; CH_2).

Preparation of the enantiomers $(-)$-$4^{2+} \cdot 2\,PF_6^-$ and $(+)$-$4^{2+} \cdot 2\,PF_6^-$: An aqueous solution of KPF_6 (100 mL, 0.5 M) was added, through a cannula, to a solution of $(-)$-$4^{2+} \cdot 2(+)$-BNP^- or $(+)$-$4^{2+} \cdot 2(+)$-BNP^- (100 mg, 39 μmol) in dichloromethane (100 mL). After 2 hours of vigorous stirring at room temperature, the organic phase was decanted, washed three times with water and dried over $MgSO_4$. After filtration, the filtrate was evaporated to dryness and the crude mixture chromatographed (Al_2O_3; eluent: $CH_2Cl_2/0-6\%$ MeOH). $(-)$-$4^{2+} \cdot 2\,PF_6^-$ or $(+)$-$4^{2+} \cdot 2\,PF_6^-$ were isolated in a quantitative yield (84 mg, 39 μmol). Their ^1H NMR spectra, showing the absence of the BNP^- ion, were similar to that of the copper(I) complex of the knot with the triflate anion.

$(-)$-$4^{2+} \cdot 2\,PF_6^-$: $[M]_D = -70000$ ($c = 5.07 \times 10^{-6}$ in CH_2Cl_2); CD (CH_2Cl_2): λ_{max} ($\Delta\varepsilon$) = 245 ($+155$), 267 ($+306$), 302 ($+179$), 335 (-640), 507 nm (-20.7)

$(+)$-$4^{2+} \cdot 2\,PF_6^-$: $[M]_D = +69000$ ($c = 4.72 \times 10^{-6}$ in CH_2Cl_2) CD (CH_2Cl_2): λ_{max} ($\Delta\varepsilon$) = 244 (-154), 266 (-306), 302 (-180), 336 ($+640$), 508 nm ($+20.8$).

Demetallation: $(-)$-5 and $(+)$-5: Potassium cyanide (0.5 g, large excess) was added to a solution of $(-)$-$4^{2+} \cdot 2\,PF_6^-$ or $(+)$-$4^{2+} \cdot 2\,PF_6^-$ (50 mg, 20 μmol) in refluxing wet acetonitrile (100 mL). The mixture was stirred at $80\,^\circ$C for 4 hours, during which time the characteristic dark-red colour of the copper(I) complex progressively disappeared. The solvent was evaporated and the residue was dissolved in dichloromethane. The crude mixture was washed three times with ammonia (0.1 M), dried over $MgSO_4$ and filtered off to give $(-)$-5 or $(+)$-5 as pale-yellow solids in quantitative yield (37 mg, 20 μmol).

$(-)$-5: $[M]_D = -19000$ ($c = 4.27 \times 10^{-6}$ in CH_2Cl_2)

$(+)$-5: $[M]_D = +20000$ ($c = 4.88 \times 10^{-6}$ in CH_2Cl_2)

^1H NMR (CD_2Cl_2, 200 MHz): $\delta = 8.80$ (dd, $^3J = 7.7$ Hz, $^4J = 1.4$ Hz, 4H; H_b), 8.72 (br s, 2H; H_a), 8.37 (d, $^3J = 8.4$ Hz, 4H; H_3), 8.28 (d, $^3J = 8.4$ Hz, 4H; H_4), 8.13 (d, $^3J = 8.7$ Hz, 8H; H_o), 8.09 (d, $^3J = 8.3$ Hz, 4H; H_7), 7.90 (d, $^3J = 8.3$ Hz, 4H; H_8), 7.68 (t, $^3J = 7.7$ Hz, 2H; H_c), 7.55 (AB, $^3J = 8.8$ Hz, 8H; H_{5-6}), 6.98 (d, $^3J = 8.7$ Hz, 8H; H_m), 4.30–3.60 (m, 48H; CH_2).

Remetallation with silver(I): $(+)$-$6^{2+} \cdot 2\,BF_4^-$ and $(-)$-$6^{2+} \cdot 2\,BF_4^-$: A solution of $AgBF_4$ (45 mg, 10 equiv) in MeOH (5 mL) was added, through a cannula, to a solution of $(-)$-5 or $(+)$-5 (37 mg, 20 μmol) in CH_2Cl_2 (30 mL). The mixture was stirred at room temperature for 12 hours. The solvent was evaporated and the residue was dissolved in dichloromethane. The crude mixture was washed three times with water, dried over $MgSO_4$, filtered and chromatographed (Al_2O_3, $CH_2Cl_2/0-2\%$ MeOH) to give $(-)$-$6^{2+} \cdot 2\,BF_4^-$ or $(+)$-$6^{2+} \cdot 2\,BF_4^-$ as colourless solids in a 95% yield.

$(-)$-$6^{2+} \cdot 2\,BF_4^-$: $[M]_D = -33000$ ($c = 5.17 \times 10^{-6}$ in CH_2Cl_2); CD (CH_2Cl_2): λ_{max} ($\Delta\varepsilon$) = 240 (-194), 262 ($+359$), 304 ($+180$), 336 nm (-760); $(+)$-$6^{2+} \cdot 2\,BF_4^-$: $[M]_D = +34000$ ($c = 5.34 \times 10^{-6}$ in CH_2Cl_2); CD (CH_2Cl_2): λ_{max} ($\Delta\varepsilon$) = 240 ($+189$), 263 (-349), 304 (-176), 335 nm ($+742$); UV/Vis (CH_2Cl_2): λ_{max} (ε): 241 (110600), 269 (79600), 311 nm (65400); ^1H NMR (CD_2Cl_2, 200 MHz): $\delta = 9.88$ (br s, 2H; H_a), 8.47 (d, $^3J = 8.4$ Hz, 4H; H_7), 8.13 (d, $^3J = 8.8$ Hz, 4H; H_4), 7.95 (AB, $^3J = 9.0$ Hz, 8H; H_{5-6}), 7.74 (d, $^3J = 8.4$ Hz, 4H; H_8), 7.37 (t, $^3J = 7.9$ Hz, 2H; H_c), 7.07 (d, $^3J = 8.6$ Hz, 8H; H_o), 7.10 (d, $^3J = 7.9$ Hz, 4H; H_b), 6.53 (d, $^3J = 8.8$ Hz, 4H; H_3), 5.85 (d, $^3J = 8.6$ Hz, 8H; H_m), 4.20–3.20 (m, 48H; CH_2).

X-ray crystal structure analysis: Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-105608. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[39] Crystal data for $C_{108}H_{96}N_8O_{14}Cu_2 \cdot 2\,PF_6 \cdot C_6H_6$: $M = 2225.14$, orthorhombic, space group $P2_12_12$, $a = 29.098$ (1), $b = 14.6590$ (5), $c = 11.7333$ (5) Å, $V = 5004.8$ (6) Å^3, $Z = 2$, $\rho_{calcd} = 1.48$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.546$ mm^{-1}. Data were collected on a Nonius Kappa CCD diffractometer with Mo$_{K\alpha}$ graphite monochromated radiation ($\lambda = 0.71073$ Å) at 173 K. A dark-red crystal of dimensions $0.23 \times 0.20 \times 0.15$ mm^3 was used and a total of 31 697 data were collected, $1.5° < \theta < 26.38°$. 3299 reflections having $I > 3\sigma(I)$ were used for structure determination and refinement. The structure was solved using direct methods and refined against $|F|$. Hydrogen atoms were introduced as fixed contributors. No absorption corrections were applied. For all computations the Nonius OpenMoleN package[42] was used. The absolute structure was determined by refining Flack's x parameter: $x = -0.02(3)$. Final results: $R(F) = 0.073$, $Rw(F) = 0.086$, $GOF = 1.656$, maximum residual electronic density = 0.61 e Å^{-3}.

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