# A [2]Catenane Containing 1,1′-Binaphthyl Units and 1,10-Phenanthroline Fragments: Synthesis and Intermolecular Energy Transfer Processes

**Masatoshi Koizumi,[a] Christiane Dietrich-Buchecker,[a] and Jean-Pierre Sauvage*[a]**

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A chiral copper(I)-complexed [2]catenane consisting of two interlocking 38-membered rings, each ring incorporating a 2,9-diphenyl-1,10-phenanthroline (dpp) and an (*S*)-1,1′-binaphthyl group, has been prepared by means of a transition metal template strategy. Demetalation afforded the corresponding free chiral [2]catenane. The coordination polyhedron of the $Cu(dpp)_2$ core in this chiral copper(I)-complexed [2]catenane reflects the distortion of the chiral 1,1′-binaphthyl units, as evidenced by the circular dichroism (CD) measurements. Emission measurements demonstrated that in the two-chromophore compounds (*S*)-**6** and (*S*,*S*)-**9**, efficient energy transfer between the 1,1′-binaphthyl component and the dpp unit takes place in solution at room temperature.



## Introduction

Catenanes are nowadays relatively accessible and their physical properties can be controlled by introducing various functionalities in their backbone or at their periphery. The chirality of catenanes and other compounds, whose molecular graph is not planar, can be topological. A limited number of topologically chiral species are known,[1] the prototype being the trefoil knot.[2] More classical is the geometrical (or Euclidian) chirality, which is based on the metric properties of the object considered. Several examples of catenanes displaying classical or topological chirality have been reported in the course of the last few years.[3] Some of these systems have even been resolved, mostly by chromatography using chiral supports.[2d,3h−3j,4]

Since the 1,1′-binaphthyl motif is one of the most important chiral groups in relation to molecular recognition[5] and asymmetric catalysis,[5,6] we planned to introduce it as a constitutive element of the rings in [2]catenanes prepared according to the $Cu^{I}$-based strategy which we have developed in the last two decades.[7]

We would now like to report that a copper(I)-complexed [2]catenane containing two optically pure 1,1′-binaphthyl groups (one in each ring) in its backbone could be prepared. Demetalation afforded a free catenane consisting of two interlocking 38-membered rings, each ring incorporating a 2,9-diphenyl-1,10-phenanthroline (dpp) and an (*S*)-1,1′-binaphthyl group. Preliminary luminescence measurements show that the binaphthyl unit acts as an energy donor, in its singlet excited state, towards the dpp fragment.

## Results and Discussion

The target chiral [2]catenane was synthesized by means of the transition metal template strategy developed and used extensively for making various catenanes, rotaxanes, and knots.[8] The general principle of construction is shown in Figure 1. The molecular precursors, macrocycle **A** (containing the chiral group) and acyclic component **B**, both incorporate the same bidentate chelating subunit. In the presence of copper(I), they lead to the exclusive formation of intermediate **C** due to the stereoelectronic preference of this $d^{10}$ transition metal cation. Reaction of **C** with the appropriate chiral linker Y−Y affords the copper(I) complex

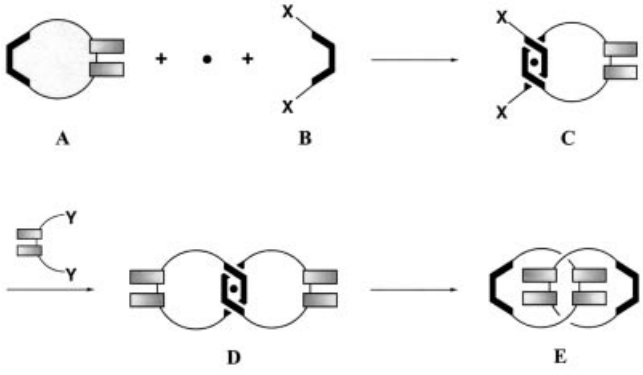


Figure 1. Transition metal template strategy for the construction of chiral [2]catenanes; thick lines represent bidentate chelates, stripes represent a chiral moiety; the black disk represents a transition metal cation; X and Y are complementary functions, such as nucleophilic and electrophilic groups

[a] Laboratoire de Chimie Organo-Minérale, UMR 7513 du CNRS, Université Louis Pasteur,
4, rue Blaise Pascal, 67070 Strasbourg, France
Fax: (internat.) + 33-3-90241368
E-mail: sauvage@chimie.u-strasbg.fr

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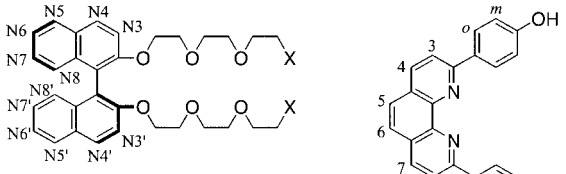
of the desired chiral catenane **D**. Finally, removal of the metal template affords the free catenane species **E**, in which the two cyclic components are held together only by a mechanical bond.

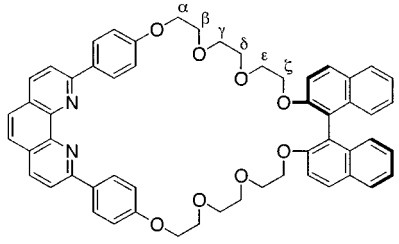
The macrocyclic and acyclic precursors, both of which contain the chiral 1,1′-binaphthyl group, are shown in Figure 2. The relatively common and cheap chiral (*S*)-1,1′-bi-2-naphthol [(*S*)-**1**] was chosen as the source of the chiral 1,1′-binaphthyl unit in the latter precursors. The 38-membered macrocycle (*S*)-**6**, containing a dpp unit as well as an (*S*)-1,1′-binaphthyl group can be obtained by two different procedures. In the first one macrocyclization occurs between 2,9-bis(4-hydroxyphenyl)-1,10-phenanthroline (**5**) and the diiodide (*S*)-**4**, prepared from (*S*)-**1** and 2-[2-(iodoethoxy)ethoxy]ethanol,[9] whereas in the second one it occurs between (*S*)-**1** and 2,9-bis(4-{2-[2-(2-iodoethoxy)-ethoxy]ethoxy}phenyl)-1,10-phenanthroline.[10] We chose the former procedure as, according to earlier work, it should afford better yields.[11]



(*S*)-**1**: 1,1′-bi-2-naphthol
(*S*)-**2**: X = OH
(*S*)-**3**: X = O*p*-$SO_2C_6H_4CH_3$
(*S*)-**4**: X = I



**5**

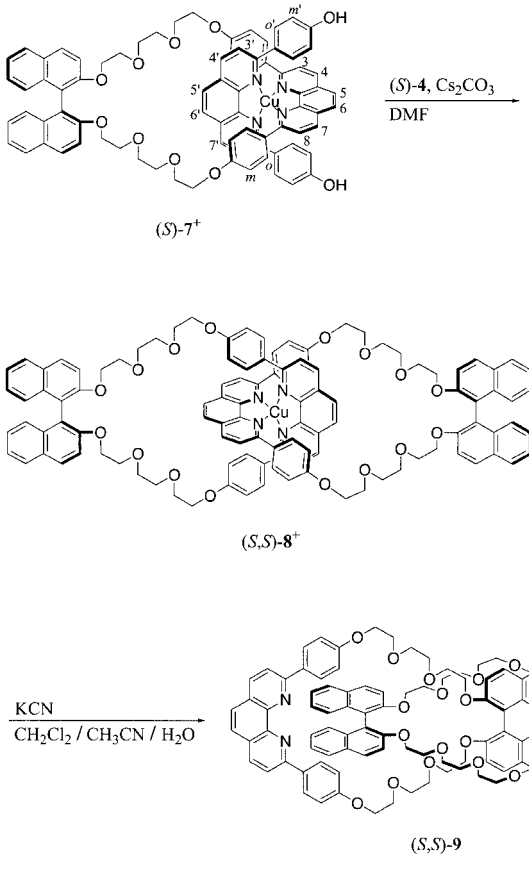


(*S*)-**6**

Figure 2. Macrocyclic and acyclic precursors; numbering in macrocycle (*S*)-**6** for dpp and 1,1′-binaphthyl units are identical to those given in its precursors

The diol (*S*)-**2** was obtained in 74% yield by reaction of (*S*)-**1** with 2-[2-(iodoethoxy)ethoxy]ethanol in the presence of $K_2CO_3$ in DMF at 100 °C.[9] The tosylation of (*S*)-**2** was achieved in 96% yield with *p*-toluenesulfonyl chloride in the presence of triethylamine in $CH_2Cl_2$. Subsequent treatment of ditosylate (*S*)-**3** with NaI in acetone gave diiodide (*S*)-**4** in 90% yield. The macrocycle (*S*)-**6** was synthesized in 35% yield by treating **5** with (*S*)-**4** under high-dilution conditions, with $Cs_2CO_3$ as a base in DMF at 55 °C.

The individual steps leading to the free [2]catenane (*S*,*S*)-**9** are depicted in Scheme 1. Precatenane (*S*)-**7**$^+$ was prepared in quantitative yield by first mixing $[Cu(CH_3CN)_4]PF_6$ and macrocycle (*S*)-**6** in $CH_3CN$/$CH_2Cl_2$ under argon and then adding a stoichiometric amount of **5** in DMF at room temperature. Its formation was accompanied by a marked color change from orange to red-brown in the final step. The precatenane (*S*)-**7**$^+$, whose structure and yield were ascertained by $^1$H NMR spectroscopy, could be used without any further purification for the final cyclization step. The latter was performed by successive addition of small batches of a $Cs_2CO_3$ suspension in DMF to the mixture of (*S*)-**4** and (*S*)-**7**$^+$ in DMF at 55 °C under argon. These additions were performed over a period of 18 h. The reaction was followed by counterion exchange ($KPF_6$) and chromatography. It afforded the desired chiral [2]catenane (*S*,*S*)-**8**$^+$ in 21% yield. Demetalation of (*S*,*S*)-**8**$^+$ to give the corresponding free [2]catenane (*S*,*S*)-**9** was accomplished by treating a solution of (*S*,*S*)-**8**$^+$ in $CH_2Cl_2$/$CH_3CN$ with a large excess of aqueous KCN at room temperature. The yield of (*S*,*S*)-**9** was 30% after chromatography. This relatively low yield compared to that of free [2]catenanes in earlier work could be caused by an incomplete extraction of the product into the organic phase due to incomplete removal of $CH_3CN$ after the reaction.




(*S*)-**7**$^+$

(*S*,*S*)-**8**$^+$

(*S*,*S*)-**9**

Scheme 1. Synthesis of the copper(I) [2]catenane and decomplexed [2]catenane

The $^1$H NMR spectra of the [2]catenane (*S*,*S*)-**8**$^+$ and the free [2]catenane (*S*,*S*)-**9** are shown, together with that of macrocycle (*S*)-**6** in Figure 3. In the spectrum of (*S*,*S*)-**8**$^+$, the signals corresponding to $H_o$, $H_m$ and $H_\alpha$ undergo strong upfield chemical shifts with respect to the single macrocycle (*S*)-**6** ($\Delta\delta = -1.09$, $-1.12$ and $-1.10$ ppm, respectively) due to the high ring-current effects. On the other hand, the spectrum of (*S*,*S*)-**9** is dramatically different from that of (*S*,*S*)-**8**$^+$, suggesting that a complete reorganization of the molecule occurs upon demetalation. Indeed, the chemical shifts for $H_o$ and $H_m$ have "normal" values ($\delta = 8.47$ and 6.95 ppm, respectively), similar to those observed for the single macrocycle (*S*)-**6** ($\Delta\delta = +0.02$ and $-0.20$ ppm, respectively). In fact, the chemical shifts of the signals corresponding to each proton of (*S*,*S*)-**9** are similar to those of (*S*)-**6**, but, interestingly, they differ in their general shapes. The resonance signals of $H_o$, $H_m$, all the protons of the phenanthroline nuclei as well as those belonging to the polyoxyethylene fragments appear very broad, which is in marked contrast with the signals observed for all previous [2]catenanes that do not contain 1,1′-binaphthyl units in their organic skeleton.[12] The present broadening suggests restricted and slow motions of the [2]catenane constitutive rings due to steric and/or electronic interaction between the rigid 1,1′-binaphthyl units incorporated in each of them and other fragments.

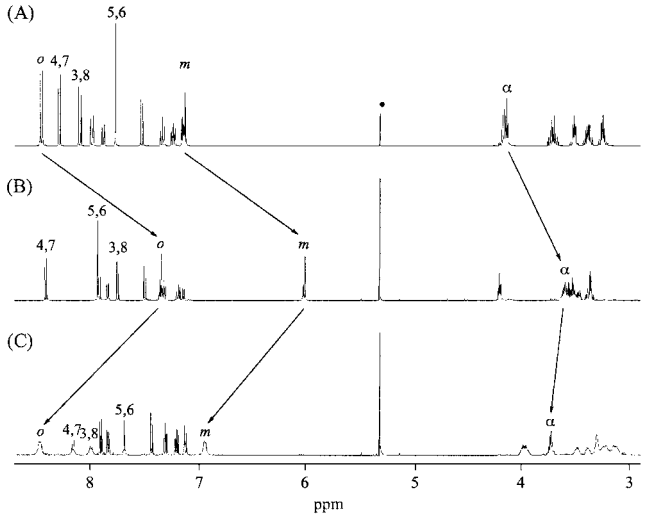



Figure 3. $^1$H NMR spectra ($CD_2Cl_2$, 25 °C) of macrocycle (*S*)-**6** (A), the copper(I) [2]catenane (*S*,*S*)-**8**$^+$ (B) and decomplexed [2]-catenane (*S*,*S*)-**9** (C); · = solvent signal

The FAB mass spectrum of the [2]catenane (*S*,*S*)-**8**$^+$ shows two peaks, the molecular ion peak at *m*/*z* = 1821.7, corresponding to the loss of one $PF_6^-$ anion, and a peak at *m*/*z* = 941.3, corresponding to the loss of one $PF_6^-$ anion and one macrocycle (*S*)-**6**. Similarly, the FAB mass spectrum of free [2]catenane (*S*,*S*)-**9** shows two peaks, the molecular ion peak at *m*/*z* = 1758.7 (protonated), as well as a peak at *m*/*z* = 879.2, corresponding to the protonated macrocycle (*S*)-**6**. As expected on the basis of earlier studies, there is no peak between the molecular ion peak and that of the single macrocycle. Such a pattern appears to be highly characteristic of catenated species.[7,13]

The circular dichroism (CD) spectra of the copper(I) [2]catenane (*S*,*S*)-**8**$^+$ and the demetalated [2]catenane (*S*,*S*)-**9** are depicted in Figure 4. As expected, positive Cotton effects were observed at 241 nm, which is the classical wavelength region of the 1,1′-binaphthyl chromophore present in both compounds [$\Delta\varepsilon = +245.3$ L·mol$^{-1}$·cm$^{-1}$ for (*S*,*S*)-**8**$^+$ and $\Delta\varepsilon = +95.9$ L·mol$^{-1}$·cm$^{-1}$ for (*S*,*S*)-**9**].[14] Much more interesting, however, are the strong negative CD ($\Delta\varepsilon$) values observed at 281 nm and 337 nm ($\Delta\varepsilon = -94.2$ L·mol$^{-1}$·cm$^{-1}$ at 281 nm and $\Delta\varepsilon = -62.7$ L·mol$^{-1}$·cm$^{-1}$ at 337 nm, respectively), for the copper(I) [2]catenane (*S*,*S*)-**8**$^+$. The latter values, clearly characteristic of the dpp chromophore, are drastically reduced in the chiroptical properties of (*S*,*S*)-**9**, which strongly suggests that the coordination polyhedron built around the copper(I) atom by the two dpp fragments in (*S*,*S*)-**8**$^+$ is chiral. Most probably, the two phenanthrolines are far from being perpendicular to one another, but rather adopt a tilted, and thus chiral, conformation. This chiral distortion observed around the copper(I) atom merely reflects the distortion caused by the chiral 1,1′-binaphthyl units, that is to say that we are seeing chirality transfer from the 1,1′-binaphthyl units to the $Cu(dpp)_2$ core. Similar chirality-transfer phenomena have been observed in various other cases as, for example, in the chiral peptide rotaxanes studied by Leigh and co-workers,[3b] chiral dendrophanes,[3j] or chiral triple helices.[15]

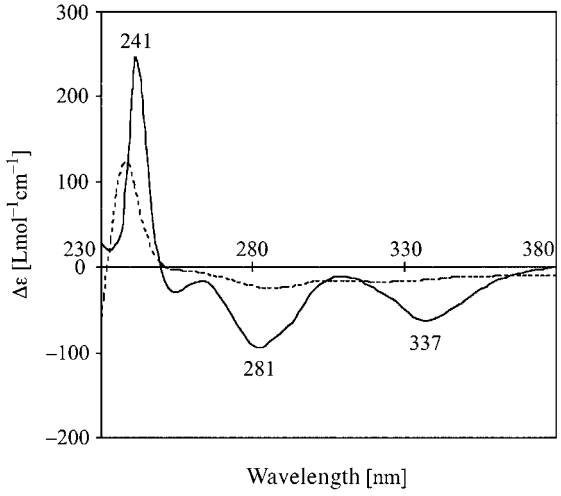



Figure 4. CD spectra of the copper(I) [2]catenane (*S*,*S*)-**8**$^+$ (continuous line) and demetalated [2]catenane (*S*,*S*)-**9** (dashed line) (230−380 nm, $CH_2Cl_2$, 20 °C)

The UV/Vis absorption spectra ($CH_2Cl_2$, room temperature; Figure 5) of the copper(I) [2]catenane (*S*,*S*)-**8**$^+$, the free [2]catenane (*S*,*S*)-**9** and a few reference compounds [the macrocycle (*S*)-**6**, (*R*)-**1** derivative (*R*)-**10** and phenanthroline derivative 2,9-bis(4-anisyl)-1,10-phenanthroline (dap)] show that the various components of the interlocking rings behave as electronically independent units. Interestingly,

emission measurements ($CH_2Cl_2$, room temperature, $\lambda_{ext}$ = 333 nm) show that interactions exist in the excited state between the 1,1′-binaphthyl unit and the dpp nucleus. 1,1′-Bi-2-naphthol (**1**) is known to be a strong emitter in the UV region.[16] Indeed, compound (*R*)-**10** emits around 360 nm. This emission is completely quenched in the macrocycle (*S*)-**6** and in compounds (*S*,*S*)-**8**$^+$ and (*S*,*S*)-**9**. Furthermore, in the copper(I)-free compounds (*S*)-**6** and (*S*,*S*)-**9**, a strong emission is observed around 400 nm, in agreement with previous observations on related compounds.[17] This emission band originates from the dpp subunit in its singlet excited state. These observations tend to indicate that efficient energy transfer takes place between the 1,1′-binaphthyl motif in its singlet excited state and the dpp nucleus in its ground state. By contrast, and as expected from the thermodynamic properties of the chromophores, no energy transfer is observed from the dpp unit.

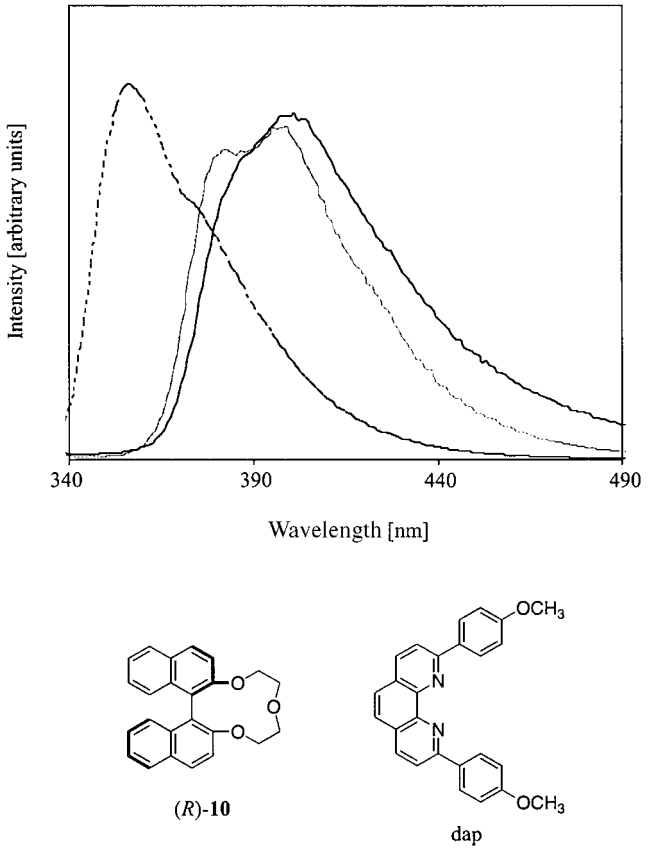



Figure 5. Emission spectra of the free [2]catenane (*S*,*S*)-**9** (continuous line) and the reference compounds (*R*)-**10** (dashed line) and dap (pale dotted line) (340−490 nm, $CH_2Cl_2$, room temperature, $\lambda_{ext}$ = 333 nm)

## Conclusion

In conclusion, a new chiral [2]catenane has been prepared using the copper(I) template approach. Each ring incorporates a dpp chelating unit and a chiral 1,1′-binaphthyl group. Removal of copper(I) affords a metal-free [2]catenane. Interestingly, CD measurements show that for the copper(I)-complexed species, chirality transfer takes place between the 1,1′-binaphthyl groups and the copper(I) complex core. In the free [2]catenane, electronic energy transfer occurs between the 1,1′-binaphthyl unit in its singlet excited state and the dpp nucleus. The copper(I) complex could find application in enantioselective electron-transfer reactions, either in its ground state or in its MLCT excited state.[18]

## Experimental Section

**General Methods:** Oxygen- or moisture-sensitive reactions were performed in oven-dried glassware attached to a vacuum line with Schlenk techniques. Dry solvents were distilled from suitable desiccants (DMF from $CaH_2$ under reduced pressure, $CH_2Cl_2$ from $P_2O_5$, $CH_3CN$ from $CaH_2$). Compound **5**[19] and $[Cu(CH_3CN)_4]PF_6$ [20] were prepared according to literature procedures. All other chemicals were purchased from commercial sources and used without further purification. Column chromatography was carried out on silica gel 60 (Merck, 70−230 mesh). Thin layer chromatography (TLC) was performed on glass plates coated with silica gel 60 $F_{254}$ (Merck). $^1$H NMR spectra were recorded with either Bruker AVANCE 300 (300 MHz), Bruker AVANCE 400 (400 MHz) or Bruker AVANCE 500 (500 MHz) spectrometers with the deuterated solvent as the lock and residual solvent as the internal reference. The numbering schemes of the protons of the [2]catenane, free [2]catenane and their precursors are indicated in Figure 2 and Scheme 1. UV/Vis spectra (absorption spectroscopy) were recorded with a Kontron Instruments UVIKON 860 spectrometer at room temperature. Fast atom bombardment mass spectra (FAB-MS) were recorded in positive-ion mode using 3-nitrobenzyl alcohol as a matrix with a ZAB-HF spectrometer. Emission spectra were recorded with an AMICO Bowman 2 spectrometer at room temperature and all solutions were saturated with oxygen-free argon. Circular dichroism (CD) spectra were recorded with a JOVIN-YVON CD VI spectrometer.

**Preparation of (*S*)-2:** (*S*)-**1** (573 mg, 2.0 mmol) was added to a vigorously stirred suspension of $K_2CO_3$ (1.38 g, 10.0 mmol) in DMF (25 mL) under a stream of argon. The temperature of the mixture was raised to 70 °C, and, after 0.5 h, 2-[2-(2-iodoethoxy)ethoxy]ethanol[9] (1.04 g, 4.0 mmol) was added by syringe. The mixture was then heated at 100 °C for an additional 20 h. DMF was removed in vacuo and the residue was taken up in $H_2O/CH_2Cl_2$. The organic layer was washed with brine and $H_2O$, dried with $MgSO_4$ and the solvents were evaporated to dryness. The crude product was purified by column chromatography on silica gel (eluent: $CH_2Cl_2$/5% $CH_3OH$) affording pure (*S*)-**2** (820 mg, 1.49 mmol) in 74% yield. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.05−3.27 (m, 8 H, C*H*$_2$O), 3.42−3.51 (m, 8 H, C*H*$_2$O), 3.60−3.63 (m, 4 H, C*H*$_2$O), 4.04−4.18 (m, 4 H, C*H*$_2$O), 7.14 (d, *J* = 8.2 Hz, 2 H, $H_{N8,8'}$), 7.21 (dd, *J* = 7.3, 8.2 Hz, 2 H, $H_{N7,7'}$), 7.32 (dd, *J* = 7.3, 8.0 Hz, 2 H, $H_{N6,6'}$), 7.41 (d, *J* = 9.1 Hz, 2 H, $H_{N3,3'}$), 7.84 (d, *J* = 8.0 Hz, 2 H, $H_{N5,5'}$), 7.93 (d, *J* = 9.1 Hz, 2 H, $H_{N4,4'}$) ppm. FAB-MS: *m*/*z* = 551.3 [M + H]; calcd. for $C_{32}H_{39}O_8$ 551.3.

**Preparation of (*S*)-3:** Triethylamine (1.5 mL, 10.8 mmol) was added at 0 °C to a solution of (*S*)-**2** (815 mg, 1.48 mmol) and tosyl chloride (852 mg, 4.5 mmol) in $CH_2Cl_2$ (30 mL). The solution was stirred at 0 °C for 1.5 h, warmed to room temperature and stirred for 5 h. $H_2O$ was then added to the solution and it was stirred at

room temperature for an additional 0.5 h. After decantation, the organic layer was washed with brine and $H_2O$, dried with $MgSO_4$ and the solvents were evaporated to dryness. The crude product was purified by column chromatography on silica gel (eluent: *n*-hexane/$C_2H_5OCOCH_3$, 1:1 to $C_2H_5OCOCH_3$) affording pure (*S*)-**3** (1.22 g, 1.43 mmol) in 96% yield. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.41 (s, 6 H, C$H_3$), 2.95−3.13 (m, 8 H, C$H_2$O), 3.41−3.47 (m, 8 H, C$H_2$O), 4.02−4.09 (m, 8 H, C$H_2$O), 7.12 (d, *J* = 8.0 Hz, 2 H, $H_{N8,8'}$), 7.19 (dd, *J* = 7.3, 8.0 Hz, 2 H, $H_{N7,7'}$), 7.29 (d, *J* = 8.4 Hz, 4 H, $H_{Ts\text{-}o}$), 7.31 (dd, *J* = 7.3, 8.0 Hz, 2 H, $H_{N6,6'}$), 7.40 (d, *J* = 8.9 Hz, 2 H, $H_{N3,3'}$), 7.76 (d, *J* = 8.4 Hz, 4 H, $H_{Ts\text{-}m}$), 7.84 (d, *J* = 8.0 Hz, 2 H, $H_{N5,5'}$), 7.92 (d, *J* = 8.9 Hz, 2 H, $H_{N4,4'}$) ppm. FAB-MS: *m*/*z* = 859.3 [M + H]; calcd. for $C_{46}H_{51}O_{12}S_2$: 859.3.

**Preparation of (*S*)-4:** A solution of (*S*)-**3** (1.22 g, 1.43 mmol) and NaI (643 mg, 4.29 mmol) in acetone (25 mL) was heated at reflux for 4 h. The solvent was then evaporated and the residue was taken up in $CH_2Cl_2/H_2O$. The organic layer was dried with $MgSO_4$, filtered, and the solvents were evaporated to afford (*S*)-**4** (994 mg, 1.29 mmol) in 90% yield. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.03−3.20 (m, 12 H, C$H_2$O), 3.46−3.58 (m, 8 H, C$H_2$O), 4.09−4.12 (m, 4 H, C$H_2$O), 7.15 (d, *J* = 8.1 Hz, 2 H, $H_{N8,8'}$), 7.22 (dd, *J* = 7.3, 8.1 Hz, 2 H, $H_{N7,7'}$), 7.33 (dd, *J* = 7.3, 7.9 Hz, 2 H, $H_{N6,6'}$), 7.42 (d, *J* = 8.8 Hz, 2 H, $H_{N3,3'}$), 7.86 (d, *J* = 7.9 Hz, 2 H, $H_{N5,5'}$), 7.94 (d, *J* = 8.8 Hz, 2 H, $H_{N4,4'}$) ppm. FAB-MS: *m*/*z* = 771.1 [M + H]; calcd. for $C_{32}H_{37}I_2O_6$ 771.1.

**Preparation of Macrocycle (*S*)-6:** A degassed mixture of (*S*)-**4** (693 mg, 0.90 mmol) and **5** (297 mg, 0.80 mmol) in DMF (80 mL) was added dropwise to a vigorously stirred suspension of $Cs_2CO_3$ (1.04 g, 3.20 mmol) in DMF (350 mL) under argon at 60 °C over 9 h. After the addition, the mixture was stirred at 60 °C for an additional 13 h. DMF was removed in vacuo and the residue was taken up in $H_2O/CH_2Cl_2$. The organic layer was washed with brine and $H_2O$, dried with $MgSO_4$ and the solvents were evaporated to dryness. The crude product was purified by column chromatography on silica gel (eluent: $CH_2Cl_2$/0.1−0.25% $CH_3OH$) followed by preparative TLC on silica (eluent: $CH_2Cl_2$/5% $CH_3OH$) affording pure (*S*)-**6** (249 mg, 0.256 mmol) in 35% yield. $^1$H NMR (400 MHz, $CD_2Cl_2$, 25 °C): δ = 3.21−3.30 (m, 4 H, $H_\delta$), 3.35−3.45 (m, 4 H, $H_\gamma$), 3.48−3.56 (m, 4 H, $H_\varepsilon$), 3.67−3.77 (m, 4 H, $H_\beta$), 4.11−4.22 (m, 8 H, $H_\alpha$ and $H_\zeta$), 7.14 (d, *J* = 9.0 Hz, 4 H, $H_m$), 7.15 (d, *J* = 7.7 Hz, 2 H, $H_{N8,8'}$), 7.24 (dd, *J* = 7.4, 7.7 Hz, 2 H, $H_{N7,7'}$), 7.34 (dd, *J* = 7.4, 8.0 Hz, 2 H, $H_{N6,6'}$), 7.53 (d, *J* = 8.9 Hz, 2 H, $H_{N3,3'}$), 7.77 (s, 2 H, $H_{5,6}$), 7.88 (d, *J* = 8.0 Hz, 2 H, $H_{N5,5'}$), 7.99 (d, *J* = 8.9 Hz, 2 H, $H_{N4,4'}$), 8.10 (d, *J* = 8.5 Hz, 2 H, $H_{3,8}$), 8.29 (d, *J* = 8.5 Hz, 2 H, $H_{4,7}$), 8.45 (d, *J* = 9.0 Hz, 4 H, $H_o$) ppm. UV/Vis ($CH_2Cl_2$, room temperature): $\lambda_{max}$ (log ε) = 285 nm (4.83), 325 (4.63). FAB-MS: *m*/*z* = 879.3 [M + H]; calcd. for $C_{56}H_{51}N_2O_8$ 879.4.

**Preparation of Precatenane (*S*)-7$^+$PF$_6^-$:** A degassed solution of $[Cu(CH_3CN)_4]PF_6$ (68.5 mg, 0.184 mmol) in $CH_3CN$ (10 mL) was transferred to a solution of (*S*)-**6** (153.7 mg, 0.175 mmol) in $CH_2Cl_2$ (10 mL) under argon. The resulting mixture immediately turned deep orange. After stirring at room temperature for 0.5 h, a solution of **5** (63.7 mg, 0.175 mmol) in DMF (8 mL) was added to the reaction mixture, turning it reddish brown. The solution was stirred under argon for 18 h. The solvent was removed in vacuo to afford pure (*S*)-**7**$^+$PF$_6^-$ in quantitative yield. (*S*)-**7**$^+$PF$_6^-$ was used without further purification. $^1$H NMR (300 MHz, $CD_2Cl_2$, 25 °C): δ = 3.38−3.66 (m, 20 H, C$H_2$O), 4.24 (t, *J* = 5.0 Hz, 4 H, $H_\zeta$), 6.02 (d, *J* = 8.7 Hz, 4 H, $H_m$), 6.04 (d, *J* = 8.8 Hz, 4 H, $H_{m'}$), 7.18 (d, *J* = 8.1 Hz, 2 H, $H_{N8,8'}$), 7.24 (dd, *J* = 7.2, 8.1 Hz, 2 H, $H_{N7,7'}$), 7.36 (dd, *J* = 7.2, 7.9 Hz, 2 H, $H_{N6,6'}$), 7.40 (d, *J* = 8.7 Hz, 4 H, $H_o$), 7.41 (d, *J* = 8.8 Hz, 4 H, $H_{o'}$), 7.54 (d, *J* = 9.0 Hz, 2 H, $H_{N3,3'}$), 7.78 (d, *J* = 8.4 Hz, 2 H, $H_{3,8}$), 7.87 (d, *J* = 8.4 Hz, 2 H, $H_{3',8'}$), 7.88 (d, *J* = 7.9 Hz, 2 H, $H_{N5,5'}$), 7.93 (s, 2 H, $H_{5',6'}$), 7.95 (d, *J* = 9.0 Hz, 2 H, $H_{N4,4'}$), 8.04 (s, 2 H, $H_{5,6}$), 8.39 (d, *J* = 8.4 Hz, 2 H, $H_{4,7}$), 8.50 (d, *J* = 8.4 Hz, 2 H, $H_{4',7'}$) ppm.

**Preparation of [2]Catenane (*S*,*S*)-8$^+$PF$_6^-$:** A degassed solution of (*S*)-**4** (141.6 mg, 0.184 mmol), (*S*)-**7**$^+$PF$_6^-$ (153.7 mg, 0.175 mmol), L-ascorbic acid (21.6 mg, 0.123 mmol) and $[Cu(CH_3CN)_4]PF_6$ (65.3 mg, 0.175 mmol) in DMF (155 mL) was heated to 55 °C. A flask containing a degassed suspension of $Cs_2CO_3$ (228.1 mg, 0.70 mmol) in DMF (25 mL) at room temperature was connected through a cannula to the flask containing (*S*)-**4** and (*S*)-**7**$^+$PF$_6^-$. A small batch (2−5 mL) of the $Cs_2CO_3$ suspension was added to (*S*)-**4** and (*S*)-**7**$^+$PF$_6^-$. Successive additions were performed over a total of 18 h. This procedure has the advantage of minimizing the partial demetallation and oxidation of (*S*)-**7**$^+$PF$_6^-$. An additional small amount of (*S*)-**4** (28.0 mg, 0.036 mmol) in DMF (2 mL) was added, and the resulting solution stirred for a further 19 h. DMF was removed in vacuo and the residue was taken up in $H_2O/CH_2Cl_2$. The organic layer was washed with brine and $H_2O$, concentrated to a volume of 20 mL, then stirred with a saturated aqueous solution of $KPF_6$ for 21 h (anion exchange). The organic layer was separated, washed with brine and $H_2O$, dried with $MgSO_4$ and the solvents were evaporated to dryness. The crude product was purified by column chromatography on silica gel (eluent: $CH_2Cl_2$/1−10% $CH_3OH$) followed by preparative TLC on silica (eluent: $CH_2Cl_2$/7% $CH_3OH$) to afford pure (*S*,*S*)-**8**$^+$PF$_6^-$ (70.1 mg, 0.036 mmol) in 21% yield. $^1$H NMR (500 MHz, $CD_2Cl_2$, 25 °C): δ = 3.35−3.41 (m, 12 H, C$H_2$O), 3.46−3.64 (m, 28 H, C$H_2$O), 4.21 (t, *J* = 5.4 Hz, 8 H, $H_\zeta$), 6.03 (d, *J* = 8.7 Hz, 8 H, $H_m$), 7.14 (d, *J* = 7.9 Hz, 4 H, $H_{N8,8'}$), 7.19 (dd, *J* = 7.3, 7.9 Hz, 4 H, $H_{N7,7'}$), 7.32 (dd, *J* = 7.3, 8.0 Hz, 4 H, $H_{N6,6'}$), 7.36 (d, *J* = 8.7 Hz, 8 H, $H_o$), 7.50 (d, *J* = 8.9 Hz, 4 H, $H_{N3,3'}$), 7.75 (d, *J* = 8.2 Hz, 4 H, $H_{3,8}$), 7.84 (d, *J* = 7.9 Hz, 4 H, $H_{N5,5'}$), 7.92 (d, *J* = 8.9 Hz, 4 H, $H_{N4,4'}$), 7.94 (s, 4 H, $H_{5,6}$), 8.41 (d, *J* = 8.2 Hz, 4 H, $H_{4,7}$) ppm. UV/Vis ($CH_2Cl_2$, room temperature): $\lambda_{max}$ (log ε) = 282 nm (4.80), 330 (4.69). FAB-MS: *m*/*z* = 1821.7 [M − $PF_6$]; calcd. for $C_{112}H_{100}CuN_4O_{16}$ 1821.6.

**Demetallation of (*S*,*S*)-8$^+$PF$_6^-$:** KCN (6.0 mg, 0.0915 mmol) in $H_2O$ (5 mL) was added to (*S*,*S*)-**8**$^+$PF$_6^-$ (36.0 mg, 0.0183 mmol) in $CH_3CN$ (7 mL). The initial reddish brown color disappeared rapidly, and the mixture was stirred at room temperature for 1 h. $CH_2Cl_2$ (5 mL) was added to the mixture and it was stirred for an additional 3 h. The colorless organic layer was separated, washed with brine and $H_2O$, dried with $MgSO_4$ and the solvents were evaporated to dryness. The crude product was purified by column chromatography on silica gel (eluent: $CH_2Cl_2$/0−4% $CH_3OH$) to afford pure (*S*,*S*)-**9** (9.5 mg, 0.0055 mmol) in 30% yield. $^1$H NMR (500 MHz, $CD_2Cl_2$, 25 °C): δ = 3.12−3.26 (br. m, 8 H, C$H_2$O), 3.31 (br. s, 4 H, C$H_2$O), 3.37−3.52 (br. m, 8 H, $H_\beta$), 3.70−3.78 (m, 8 H, $H_\alpha$), 3.94−4.03 (m, 8 H, $H_\zeta$), 6.95 (br. d, 8 H, *J* = 7.2 Hz, $H_m$), 7.12 (d, *J* = 8.9 Hz, 4 H, $H_{N8,8'}$), 7.21 (dd, *J* = 7.3, 8.9 Hz, 4 H, $H_{N7,7'}$), 7.31 (dd, *J* = 7.3, 7.8 Hz, 4 H, $H_{N6,6'}$), 7.44 (d, *J* = 8.9 Hz, 4 H, $H_{N3,3'}$), 7.69 (s, 4 H, $H_{5,6}$), 7.84 (d, *J* = 7.8 Hz, 4 H, $H_{N5,5'}$), 7.91 (d, *J* = 8.9 Hz, 4 H, $H_{N4,4'}$), 8.00 (br. d, 4 H, *J* = 8.4 Hz, $H_{3,8}$), 8.16 (br. d, 4 H, *J* = 8.4 Hz, $H_{4,7}$), 8.47 (br. d, 8 H, *J* = 7.2 Hz, $H_o$) ppm. UV/Vis ($CH_2Cl_2$, room temperature): $\lambda_{max}$ (log ε) = 284 nm (5.18), 324 (5.00). FAB-MS: *m*/*z* = 1758.7 [M + H]; calcd. for $C_{112}H_{101}N_4O_{16}$ 1758.7.

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