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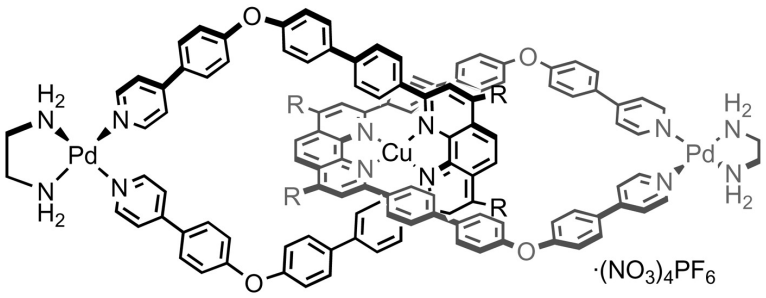

R = H, *n*-C_6H_{13}

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Quantitative Formation of [2]Catenanes Using Copper(I) and Palladium(II) as Templating and Assembling Centers: The Entwining Route and the Threading Approach

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Contribution from the Laboratoire de Chimie Organo-Minérale, UMR 7513 du CNRS, Université Louis Pasteur, Faculté de Chimie, 4, Rue Blaise Pascal, 67070 Strasbourg Cedex, France, Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo, and CREST, Japan Science and Technology Corporation (JST), Genesis Research Institute, Inc., 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan, Dankook University, 8 Hannam-dong, Yongsan-ku, Seoul 140-714, Korea, and Chemical Analysis Center, Chiba University, Yayoicho, Inage-ku, Chiba 263-8522, Japan

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Abstract: Transition metal-mediated templating and self-assembly have shown powerful potentials for the synthesis of interlocked molecules. These two strategies were combined in designing and preparing a new type of coordination catenanes incorporating Cu(I) and Pd(II) metal centers. The ligand designed here contains a phenanthroline core and pyridine sidearms (compound **1**). Using this phenanthroline-pyridine conjugated ligand, two approaches were examined, which were shown to be surprisingly efficient for the catenane synthesis: the entwining route (entwining of two ligands around Cu(I) followed by Pd(II) clipping) and the threading approach (Cu(I)-templated threading of a cyclic ligand on an acyclic ligand followed by the Pd(II) clipping of the second ring). In the former method, stepwise treatment of **1** with $Cu(CH_3CN)_4PF_6$ (templating center) and $enPd(NO_3)_2$ (assembling center) gives rise to the quantitative formation of $CuPd_2$ catenane **18**. In the latter method, Cu(I) templates the threading of phenanthroline-containing macrocycle **2** on ligand **1**, which is followed by Pd(II) clipping to give hetero catenane **20**. In both approaches, the formation of catenanes is convincing thanks to the strong templating effect of Cu(I), while the ring closure steps are efficiently furnished by Pd(II)-directed self-assembly.

Introduction

Interlocking ring systems (catenanes) and threaded rings (rotaxanes) are presently attracting much attention in relation to their topological, electronic, and dynamic properties.[1−3] In particular, they represent promising prototypes of switches, machines, and motors at the molecular level.[4−7]

Catenanes have mostly been restricted to organic chemistry since, traditionally, their backbones consisted of covalent bonds (usually C−C, C−O, or C−N bonds). In addition, these species were normally not obtained under thermodynamic control: the cyclization reaction(s) representing the last step(s) had no reversibility character.

The situation changed dramatically when catenanes started to be prepared using reversible reactions as ring-closing steps. Coordination chemistry bonds such as Pd(II)−N bonds (N being a pyridine nitrogen atom) turned out to be particularly well adapted to the formation of cyclic structures and, in particular, interlocking rings, under thermodynamic control.[8] Organic chemistry bonds whose formation and cleavage is reversible have also been used to generate catenanes or rotaxanes.[9]

Transition metals have been incorporated as constitutive elements in various types of catenanes.[10] Another case relies on a Grignard reagent, which allowed the preparation of a Mg^{2+}-incorporating catenane.[11] Of course, transition metals have also

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‡ The University of Tokyo.
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|| Genesis Research Institute, Inc.
Dankook University.
⊥ Chemical Analysis Center, Chiba University.

(1) For early work, see: Schill, G. *Catenanes, Rotaxanes and Knots*; Academic Press: New York, 1971.
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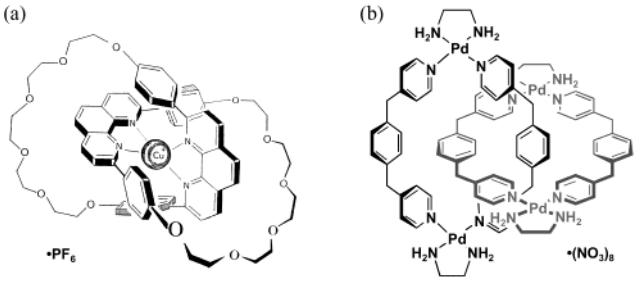

Figure 1. Two prototypes of catenanes, prepared by the Strasbourg group (a) or the Chiba−Okazaki−Nagoya−Tokyo team (b).

played another important role in catenane chemistry. They afforded particularly efficient templates, allowing high yields of the precursors.[12] Copper(I) has been used extensively to gather and orient the various organic fragments to be incorporated in the catenane. Very generally, the last cyclization step leading to the desired interlocking ring system used to be a classical nonreversible reaction (Williamson ether formation reaction or Glaser−Egglinton oxidative coupling of terminal acetylenic groups). The only exception of a reversible organic reaction used in conjunction with transition metal-templated synthesis of catenanes makes use of the ring-closing metathesis of olefins.[13]

The present report describes the use of transition metal centers both as elements of the rings and as template. This approach relies on previous work from our two groups ("template"[12] and "self-assembly"[14]), and it involves thermodynamic control for both processes: (i) formation of the precursor to be cyclized and (ii) ring-closing reaction. Preliminary data have been briefly described as communications.[15] We will focus in the present paper on the synthesis of [2]catenanes constructed around copper(I) complexes used as scaffolds and cyclized using palladium(II).

Results and Discussion

Design of the Ligands and Strategy. The two prototypical catenanes synthesized by our groups are represented in Figure 1. The copper(I)-complexed interlocking system (a) is an example of a catenane prepared using a transition metal center as template.[12] It consists of two interlocking 30-membered rings. The 4-palladium compound (b) is the first catenane obtained via self-assembly. It is formed quantitatively under thermodynamic control,[8] and it also consists of two interlocking 30-membered rings.

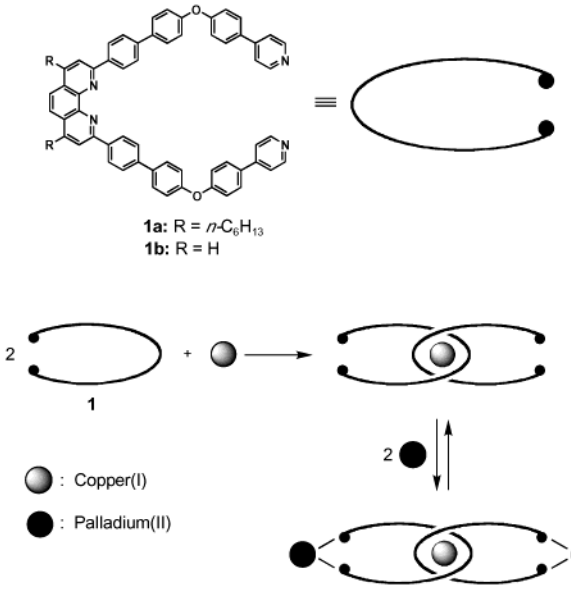

Figure 2. The entwining approach: the two organic fragments (**1**) are first coordinated to copper(I) so as to afford an entwined complex. The double ring closing step is performed using palladium(II) as a "clipping" metal center.

We have previously prepared a doubly interlocking [2]-catenane using copper(I) as a gathering metal, able to induce the entwining of two organic fragments, followed by a complex cyclization step with palladium(II).[15] Unexpectedly, the simple catenane was not obtained because the organic ligands were too short to afford rings incorporating single palladium(II) atoms. The dimeric compound, i.e., the 4-crossing [2]catenane, was obtained instead of the simple system, in agreement with molecular modeling studies that indicated very clearly that the doubly interlocking compound was the most stable. In the present work, to minimize ring strain, we used a large organic ligand, which was expected to afford nonstrained Pd(II)-containing rings.

Two distinct strategies have been followed: (i) the "entwining" strategy, consisting in intertwining the two organic fragments around Cu(I) before closing the rings with Pd(II), and (ii) the "threading" approach, with relies on the copper(I)-directed threading of a presynthesized ring by a coordinating organic fragment, followed by clipping two appended coordinating groups by Pd(II) so as to form the second ring. The two strategies and the chemical structures of the organic precursors used are represented in Figures 2 and 3.

Synthesis of 1a Using the Ullman Reaction. Ligand **1a** was obtained by a double Ullman reaction[16] between 4,7-di-*n*-hexyl-2,9-bis[4-(4-hydroxyphenyl)phenyl]-1,10-phenanthroline (**3**)[17] and 4-(4-bromophenyl)pyridine (**4**).[18] The latter reaction was

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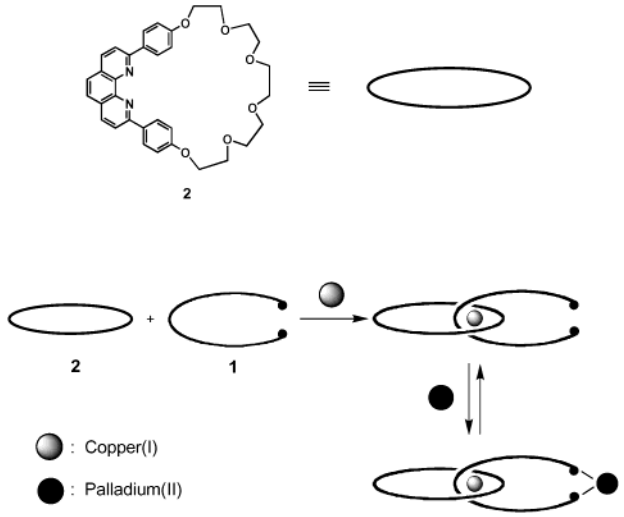
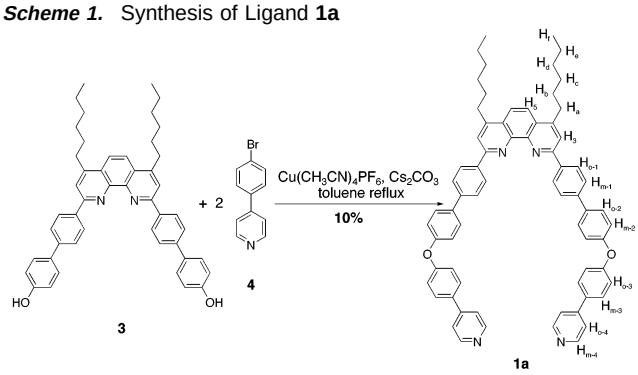


Figure 3. The threading approach: the open-chain ligand is threaded through the ring (**2**) thanks to the gathering and threading effect of copper(I). The single cyclization step with palladium(II) is carried out as in Figure 2.

Scheme 1. Synthesis of Ligand **1a**



performed in refluxing toluene in the presence of Cs_2CO_3 and $Cu(CH_3CN)_4 \cdot PF_6$ over 3 days. After demetalation of the crude reaction mixture with KCN and purification by chromatography over silica gel, **1a** was obtained in 10% yield as a pale yellow glass (Scheme 1). It could be fully characterized by ^{1}H NMR and mass spectroscopy.

Synthesis of 1b Using Carbon−Carbon Bond Formation via Stille Cross-Coupling Reaction. The overall yield in the synthesis of **1a** is limited by the very low yield of the last step consisting of the Ullman reaction. To avoid this reaction, the synthesis of **1b** was centered around the commercially available diphenyl ether moiety (Scheme 2). Thus, 4-bromodiphenyl ether **5** was treated with 4-pyridylboronic acid pinacol ester (**6**, 0.5 equiv to **5**) under Suzuki−Miyaura cross-coupling conditions to give **7** in 56% yield as colorless microcrystals.[19] The bromide **7** was converted into stannyl compound **8** in 84% yield by lithiation (*n*-BuLi) followed by stannylation (Me_3SnCl). Simultaneous introduction of the two *p*-bromophenyl groups in the 2 and 9 positions of the phenanthroline could not be envisaged due to the presence of reactive bromine in the target compound. Nevertheless, the difunctionalized phenanthroline **10** could be obtained in a two-step synthesis that corresponds to two successive monosubstitution reactions performed with *p*-bromophenyllithium at low temperature. Thus 1,10-phenanthroline was treated with *p*-bromophenyllithium in diethyl ether at 0 °C to afford the 2-(*p*-bromophenyl)-1,10-phenanthroline **9** in 82% yield after hydrolysis and oxidation by MnO_2. Phenanthroline **10** was prepared by reacting **9** again with *p*-bromophenyllithium in monosubstitution conditions;[20] **10** was obtained as a white solid in 88% yield. Finally, **8** was cross-coupled with **10** under modified Stille conditions[21] ($[PdCl_2(PPh_3)_2]$/LiCl, toluene, 120 °C) to give ligand **1b** in 45% yield as a colorless solid.[18]

Synthesis of 1b Using Carbon−Carbon Bond Formation via Suzuki−Miyaura Cross-Coupling Reactions. To avoid the use of toxic Me_3SnCl and to improve the overall yield, we further studied an alternative approach to **1b**. Consequently, we succeeded in replacing the Stille coupling step by Suzuki−Miyaura coupling reaction with significant increase in chemical yield. The synthesis of bromide **7** was also slightly modified. Thus, 4-bromodiphenyl ether (**11**) was quantitatively converted to 4-bromo-4′-iododiphenyl ether (**12**) using iodine monochloride in refluxing acetic acid.[22] By taking avantage of the fact that lithiation of compound **12** should occur selectively at the C−I bond, it was treated with 1 equiv of *n*-BuLi in Et_2O in the presence of TMEDA[23] at −78 °C, and the resulting mixture was quenched with trimethylborate. After hydrolysis, the free boronic acid was used without any purification in the next step, which consists of esterification with 2,2-dimethylpropan-1,3-diol. The boronic ester **13** was obtained in 70% yield. Classical conditions for a Suzuki−Miyaura cross-coupling reaction ($[Pd(PPh_3)_4]$, Na_2CO_3 (2 M), in toluene/water at reflux) were used to react the boronic ester **13** with 4-bromopyridine hydrochloride (**14**), which was deprotonated in situ.[19] Controlling the duration of this reaction was very important since after 2 h the reaction was probably complete, but beyond, the product underwent a debromination. It also appeared that the C−Br bond of the pyridine was more reactive than that of the diphenyl ether moiety. Thus, the 4-bromo-4′-pyridyldiphenyl ether (**7**) was obtained in 80% yield. Several attempts were made to synthesize the 4-boronic-4′-pyridyldiphenyl ether (**16**): *n*-BuLi as well as *t*-BuLi did not afford satisfactory results. However, the use of pinacolato-diboron **15** with **7** in the presence of KOAc and a catalytic amount of $[Pd(dppf)]Cl_2$ (dppf is 1,1′-bis(diphenylphosphino)ferrocene) in dioxane was very efficient, as the boronic ester **16** was obtained in 95% yield.[24] The last step required the formation of two carbon−carbon bonds. Once again, classical conditions for Suzuki cross-coupling reaction were used, leading to **1b** in 80% yield on the gram scale.

Synthesis of [2]Catenanes from Three Components: The Entwining Route. As a common approach, we first examined the stepwise synthesis of Cu(I)Pd(II) bimetallic catenane **18** from ligand **1** according to the route of Figure 2, which involves the entwining of ligand **1** around a Cu(I) templating center followed by Pd(II)-mediated ring closure (the entwining route). ^{1}H NMR spectroscopy showed that both steps proceeded very cleanly. On complexation with $Cu(CH_3CN)_4 \cdot PF_6$ (0.5 mol equiv), two

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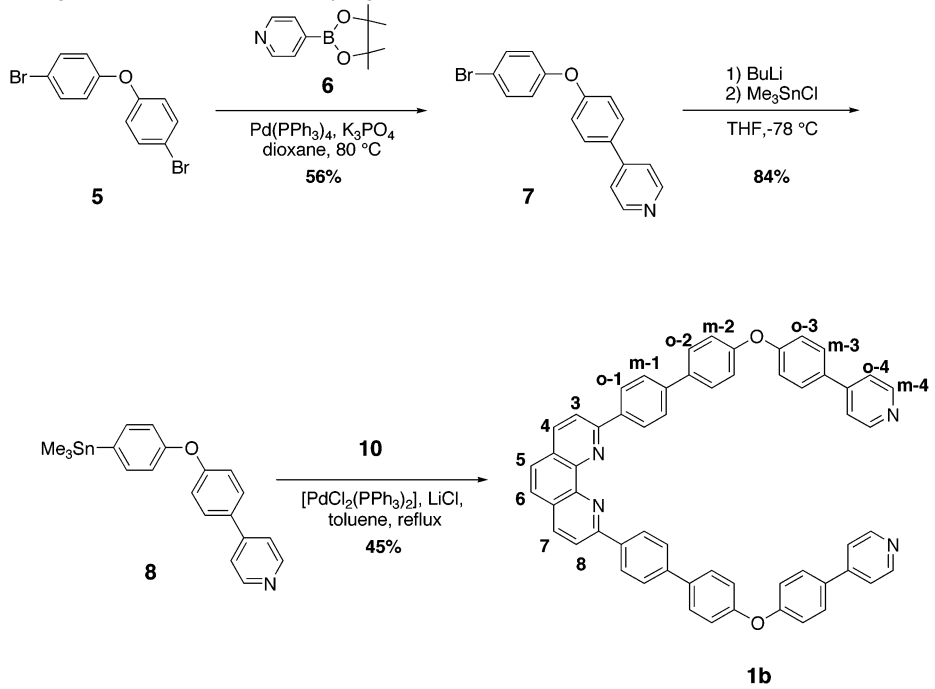
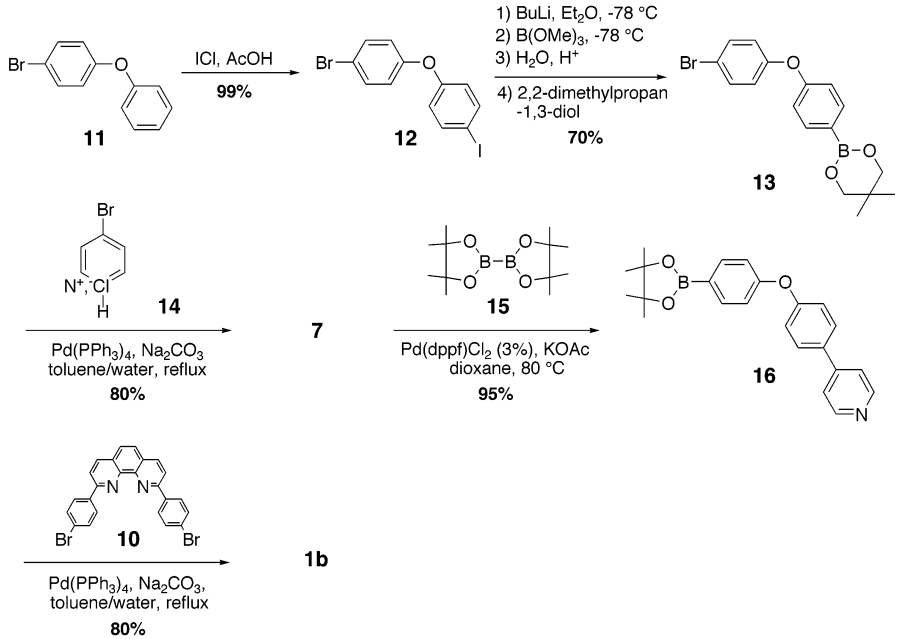
Scheme 2. Synthesis of Ligand **1b** via Stille Cross-Coupling Reaction



Scheme 3. Synthesis of Ligand **1b** via Suzuki−Miyaura Cross-Coupling Reactions



ligands are orthogonally oriented around the Cu(I) center being magnetically shielded by each other. Experimentally, ligand **1b** was suspended in a DMF solution of the Cu(I) salt (Scheme 4). A clear red solution resulted after 15 min. In ^{1}H NMR, H_{m-1} and H_{o-1} are positively shielded by the phenanthroline core, while $H_{3,8}$ and $H_{4,7}$ are negatively shielded (Figure 4b), as we have previously observed in related catenane precursors.[25] Pyridine protons (H_{m-4} and H_{o-4}) are missing probably due to acid−base interaction with (wet) solvent on the NMR time scale.

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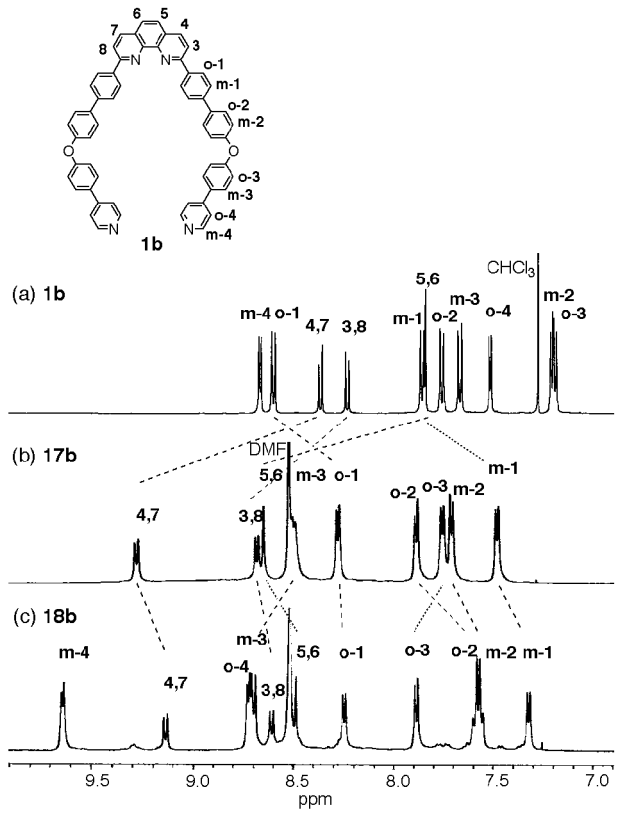
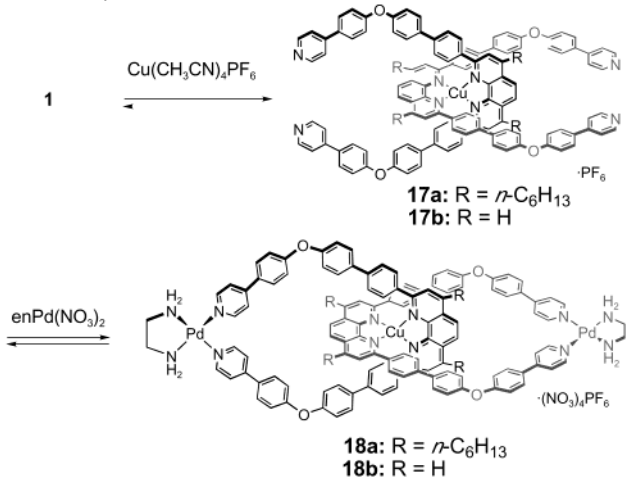


Figure 4. ^{1}H NMR observation for the preparation of catenane **18b** via entwining route (aromatic region, 500 MHz, 25 °C, 10 mM, TMS as an external standard): (a) ligand **1b** in $CDCl_3$; (b) Cu(I) complex **17b** from **1b** and $Cu(CH_3CN)_4{\cdot}PF_6$ in DMF-d_7; (c) [2]catenane **18b** from **17b** and $enPd(NO_3)_2$ in DMF-d_7.

Scheme 4. Synthesis of [2]Catenane and Its Precursor from Three Components



By adding diethyl ether to the solution, Cu(I) complex **17b** was precipitated in a pure form in 93% yield as a red microcrystalline solid.

The precursor **17b** was subsequently treated with $enPd(NO_3)_2$ for the ring-closure step. On complexation, signals are in general upfield shifted except for H_{m-3} and H_{o-3}, which are conformationally free before complexation but fixed after complexation at the negative-shielding region of the phenanthroline core of another ligand (Figure 4c). From the solution, Cu(I)Pd(II) complex **18b** was precipitated as a reddish purple powder in 92% yield by adding a large amount of diethyl ether. Although the melting point of complex **17b** was relatively low (191−192 °C), after clipping by Pd(II) ion, **18b** was not molten and decomposed even at 300 °C, indicating the rigid and highly charged catenane structure.

In addition to satisfactory NMR, CSI-MS (coldspray ionization mass spectrometry)[26] also supported the structures of **17b** and **18b**. For complex **17b**, a clear spectrum with an intense peak at *m*/*z* 1708, which corresponds to single charged $[\mathbf{17b}-PF_6]^+$, was obtained. CSI-MS of **18b** (CH_3CN-DMF, 20 mM) showed predominant peaks for multicharged $[(\mathbf{18b}-PF_6-(NO_3)_n)+(dmf)_m]^{(n+1)+}$: e.g., *m*/*z* 546.5 $[(\mathbf{18b}-PF_6-(NO_3)_3)+(CH_3CN)_2]^{4+}$, 721.6 $[\mathbf{18b}-PF_6-(NO_3)_2]^{3+}$.

As previously communicated,[15b] the same strategy was applied to the synthesis of alkyl chain-attached catenane **18a** from ligand **1a**. The catenane precursor **17a** was efficiently obtained by treating ligand **1a** with $Cu(CH_3CN)_4{\cdot}PF_6$ (Scheme 4). In contrast to **1b**, ligand **1a** showed good solubility in DMF, and the complexation in CH_3CN-DMF (1:1) solution immediately completed upon addition of $Cu(CH_3CN)_4{\cdot}PF_6$. The formation of **17a** as a single product was confirmed by NMR and CSI-MS studies. The proton NMR spectrum of **17a** in CD_3CN-DMF-d_7 showed eight signals in the aromatic region. Again, pyridine protons are too broadened to be observed. A parent peak at *m*/*z* 2046.2 in CSI-MS was assigned as $[\mathbf{17a}-PF_6]^+$. [2]Catenane **18a** was quantitatively formed by adding 2 equiv of $enPd(NO_3)_2$ into the CH_3CN-DMF solution of **17a** in the same way as those for the complexation of **18b**. This product was assigned as catenane **18a** on the basis of NMR and CSI-MS studies. CSI-MS of **18a** (CH_3CN-DMF, 20 mM) showed predominant peaks for multicharged $[(\mathbf{18a}-PF_6-(NO_3)_n)+(dmf)_m]^{(n+1)+}$: e.g., *m*/*z* 548.4 $[(\mathbf{18a}-PF_6-(NO_3)_4)+(dmf)_5]^{5+}$, 646.7 $[(\mathbf{18a}-PF_6-(NO_3)_3)+(dmf)_2]^{4+}$, 834.5 $[\mathbf{18a}-PF_6-(NO_3)_2]^{3+}$ (Figure 5a). From the red reaction solution, **18a** was isolated as red microcrystals by adding a large amount of diethyl ether (85%). While previous Pd(II)-linked catenanes that are interlocked through hydrophobic interactions are dissociated into monomer rings at low concentrations,[8a,14] catenane **18a** is considerably stable even at very low concentration (0.005 mM) because two rings are held by a Cu(I)-templating center. We note that, even under MS conditions, dissociation of **18a** into a monomeric ring (en(Pd)·$\mathbf{17a}^{3+}$ species) was not observed, consistent with the high stability of catenane **18a**.

Synthesis of a Hetero [2]Catenane from Four Components: The Threading Approach. We next examined the synthesis of hetero [2]catenane **20**, which consists of a covalent ring and a Pd(II)-clipped ring. This catenane is prepared by the "threading approach", which includes the threading of preformed macrocycle **2**[27] on ring precursor **1b** by Cu(I) templating followed by the closure of the second ring by Pd(II) clipping (Scheme 5).

The catenane precursor **19** was obtained by treating ligands **1b** and **2** with $Cu(CH_3CN)_4{\cdot}PF_6$ (1:1:1 molar ratio) in DMF (2 mL) (Scheme 5). As expected, the exclusive formation of threaded precursor **19** was observed by NMR (Figure 6b). The selective formation of **19** is driven by the impossible homo complexation of cyclic **2** (i.e., $Cu{\cdot}(\mathbf{2})_2$ formation), as well documented in our previous studies.[12] The proton NMR

(26) Sakamoto, S.; Fujita, M.; Kim, K.; Yamaguchi, K. *Tetrahedron* **2000**, *56*, 955. (b) Yamaguchi, K.; Sakamoto, S.; Imamoto, T.; Ishikawa, S. *Anal. Sci.* **1999**, *15*, 1037.
(27) Dietrich-Buchecker, C.; Sauvage, J.-P. *Tetrahedron* **1990**, *46*, 503.

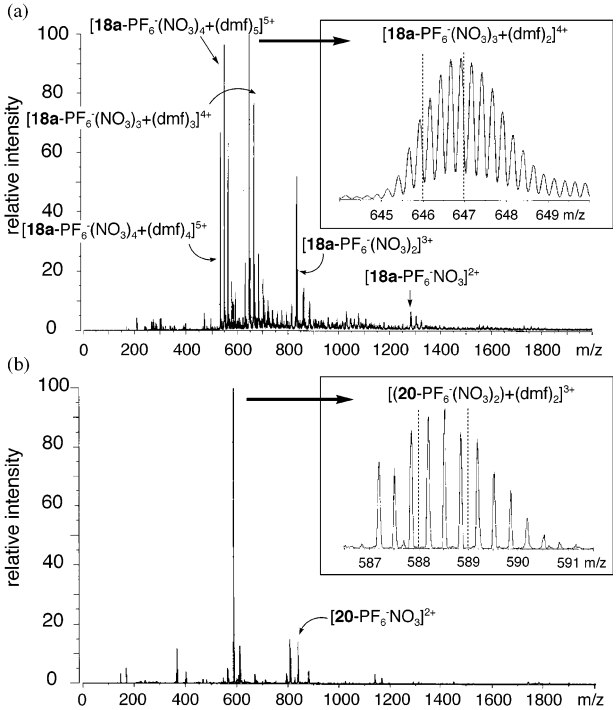
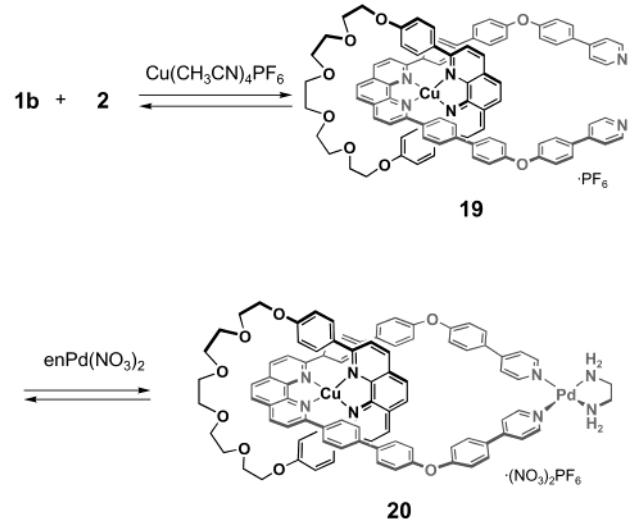


Figure 5. CSI-MS spectra of (a) **18a** and (b) **20** (high resolution).

Scheme 5. Synthesis of [2]Catenane and Its Precursor via Threading Pathway from Four Components



spectrum of **19** in DMF-d_7 showed 14 signals in the aromatic region, five from ring **2**, and nine from **1b** (pyridine protons are again missing). Chemical shift changes on complexation are reasonable: downfield shifting of protons on the phenanthroline core and upfield shifting of protons on phenylene H_{m-1} and H_{o-1} of **1b** and $H_{m'}$ and $H_{o'}$ of **2**. CSI-MS also confirmed the structure of **19** with a parent ion peak at *m*/*z* 1451.9, which is assigned as $[\mathbf{19}-PF_6]^+$. From the solution, Cu(I) complex **19** was precipitated as a purple powder in 95% yield by adding a large amount of diethyl ether.

Subsequently, [2]catenane **20** was quantitatively formed by adding enPd$(NO_3)_2$ (1 mol equiv) to the DMF solution of **19**. Again, the NMR spectrum was in good agreement with the structure of the desired [2]catenane **20** (Figure 6c). CSI-MS of **20** in a MeCN−DMF solvent also fully supported the structure by a prominent peak at *m*/*z* 588.5 $[(\mathbf{20}-PF_6-(NO_3)_2)+(dmf)_2]^{3+}$

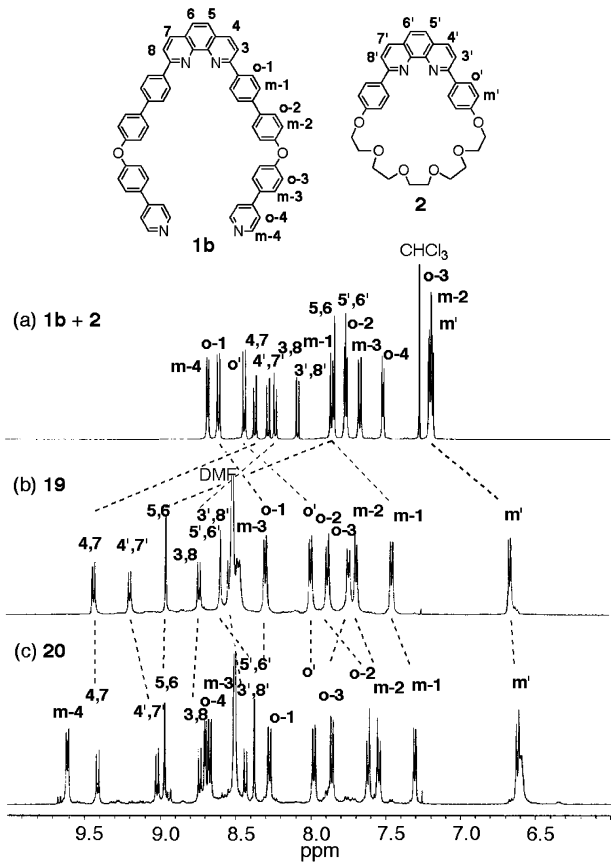


Figure 6. ^{1}H NMR observation for the preparation of catenane **20** via threading route (aromatic region, 500 MHz, 25 °C, 10 mM, TMS as an external standard): (a) a mixture of ligand **1b** and m-30 **2** in $CDCl_3$; (b) Cu(I) complex **19** from **1b**, **2**, and Cu$(CH_3CN)_4$·PF_6 in DMF-d_7; (c) [2]-catenane **20** from **19** and enPd$(NO_3)_2$ in DMF-d_7.

(Figure 5b). Addition of diethyl ether to the solution precipitated Cu(I)Pd(II) catenane **20** as a brown powder in 85% yield.

Both Cu(I)-templating and Pd(II)-clipping steps proceed under thermodynamic control. Therefore, catenane **20** is expected to be generated quantitatively regardless of the order of the events. Thus we also examined the one-step synthesis of **20** by mixing all the required components at once. Namely, **1b**, **2**, Cu$(CH_3CN)_4$·PF_6, and enPd$(NO_3)_2$ were combined in 1:1:1:1 stoichiometry in DMF at room temperature. Surprisingly, the one-step synthesis was very efficient, and after 15 min, the NMR of the resulting mixture clearly showed the quantitative formation of the same product (catenane **20**) as a single product. This result demonstrates that, under thermodynamic control, two different metal centers (Cu(I) and Pd(II)) are selectively coordinated by their most suitable coordination sites (phenanthroline and pyridine, respectively). This very high site-selectivity is ascribed to the remarkable stability of Cu$(phen)_2$ type coordination, which allows the predominant coordination of the phenanthroline sites on Cu(I) and subsequent interaction of the Pd(II) center with pyridine residues.

Conclusions

Two distinct strategies (templating and self-assembly) were combined in designing and preparing a new type of coordination catenane incorporating Cu(I) and Pd(II) metal centers. Two approaches were examined and shown to be surprisingly

efficient: the entwining route (entwining of two ligands on the Cu(I) template followed by Pd(II) clipping) and the threading approach (Cu(I)-templated threading of a cyclic ligand on an acyclic ligand followed by the Pd(II) clipping of the second ring).

It is particularly interesting that the two powerful strategies, templating and self-assembly, are complementary to each other. While the templating method is quite predictable and convincing for catenane synthesis, it requires two reaction steps (templating followed by ring closure), and the yield in the latter step is not always quantitative. On the other hand, the self-assembly method is effective for the quantitative synthesis of catenanes in a single-step reaction, but this method is not always predictable and reliable. By combining these two strategies, we have established a more powerful method for catenane synthesis. The formation of the present Cu(I)/Pd(II) catenanes is highly predictable and convincing thanks to the efficient Cu(I)-templating effect, while it can be furnished in a single step in quantitative yields by taking advantage of Pd(II)-directed self-assembly.

Experimental Section

General Procedures. All chemicals were of the best commercially available grade and used without further purification. Ethylenediamine was used for the *cis*-protection of Pd(II), as described earlier, to obtain (en)Pd(NO_3)$_2$.[28] Dry solvents were distilled from suitable desiccants (Et_2O from Na/benzophenone, dioxane from Na/benzophenone). TMEDA was dried over NaH under argon for a night and filtered through an alumina column. Column chromatography was performed with silica gel 60 (Merck 9385, 230−400 mesh) or aluminum oxide 90 (neutral, act. II−III, Merck 1097). ^{1}H and ^{13}C NMR spectra for ligands were recorded on either a Bruker WP 200 SY (200 MHz) or a AC 300 (300 MHz) spectrometer with deuterated solvent as the lock and residual solvent as the internal reference. ^{1}H NMR spectra for complexes **17**−**20** and part of the ligand were recorded on a Bruker DRX 500 spectrometer: these data were collected at ambient temperature unless otherwise noted, and the chemical shift values reported here are with respect to external TMS standard; ^{13}C NMR, H−H COSY, H−H NOESY, and C−H COSY spectra were recorded on a Bruker AMX 500 spectrometer. Deuterated solvents were acquired from Cambridge Isotopic Laboratories, Inc., and used as such for the complexation reactions and NMR measurements. Infrared spectra were recorded on a Shimadzu FTIR-8300 spectrometer with samples in compressed KBr disks. Mass spectra were obtained on a ZAB-HF spectrometer (FAB) and on a Waters Integrity TM system coupled with a Thermabeam TM mass detector (EI). CSI-MS data were measured on a four-sector (BE/BE) tandem mass spectrometer (JMS-700T, JEOL) equipped with a CSI source. Melting points were determined on a Yanaco MP-500.

4,7-Di-*n*-hexyl-2,9-bis[4′-(4-pyridyl-4-phenoxy)biphenyl]-1,10-phenanthroline (1a). 4,7-Di-*n*-hexyl-2,9-bis[4-(4-hydroxyphenyl)-phenyl]-1,10-phenanthroline (**3**, 416 mg, 0.6 mmol), 4-(4-bromophenyl)-pyridine (**4**, 234 mg, 1.0 mmol), Cu(CH_3CN)$_4$·PF_6 (113 mg, 0.3 mmol), Cs_2O_3 (652 mg, 0.5 mmol), and 450 mg of crushed activated 4 Å molecular sieves were poured, under argon and in the solid state, into a 50 mL three-necked round-bottomed flask. These solids were subsequently covered with 3 mL of anhydrous toluene. The resulting suspension was refluxed (110 °C) under argon during 72 h (5 mL of toluene and 2 mL of dimethylformamide were added after 24 h to the mixture in order to allow reasonable stirring). Thereafter solvents were evaporated to dryness, and the almost black gummy residue was taken up in a mixture of CH_2Cl_2, MeCN, and MeOH and submitted to an anion exchange with a saturated KPF_6−H_2O solution. After decantation of the water layer, the remaining dark red organic phase was stirred overnight with 800 mg of wet KCN at room temperature. Progressive disappearance of the initial red color could be observed. Once the demetalation was complete, the pale yellow suspension was evaporated to dryness and taken up in pure H_2O, which afforded a yellow precipitate. The latter was filtered on a filter paper and carefully washed with water (discard KCN). The 498 mg of yellow solid, obtained upon drying on a porous dish in air, was submitted to repetitive column chromatographies (silica gel, CH_2Cl_2−1% MeOH as eluent) to afford in 10% yield pure **1a** as a pale yellow glass (49.5 mg, 0.05 mmol). ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.66 (d, 4H, H_{m-4}, J = 6.2 Hz), 8.59 (d, 4H, H_{o-1}, J = 8.6 Hz), 8.07 (s, 2H, $H_{5,6}$), 8.03 (s, 2H, $H_{3,8}$), 7.84 (d, 4H, H_{m-1}, J = 8.4 Hz), 7.75 (d, 4H, H_{o-2}, J = 8.6 Hz), 7.66 (d, 4H, H_{m-3}, J = 8.8 Hz), 7.52 (d, 4H, H_{o-4}, J = 6.2 Hz), 7.19 (d, 4H, H_{m-2}, J = 8.6 Hz), 7.18 (d, 4H, H_{o-3}, J = 8.8 Hz), 3.23 (t, 4H, H_a, J = 7.6 Hz), 1.88 (m, 4H, H_b), 1.52 (m, 4H, H_c), 1.39 (m, 8H, H_{d+e}), 0.92 (m, 6H, H_f, J = 6.8 Hz). MS (FAB): m/z 991.2 (MH^+).

4-[4-(4-Bromophenoxy)phenyl]pyridine (7). 4-Bromophenyl ether (**5**, 6.40 g, 19.5 mmol), 4-pyridylboronic acid pinacol ester (**6**, 2.00 g, 9.75 mmol), K_3PO_4 (2.49 g, 11.7 mmol), and [Pd(PPh_3)$_4$] (300 mg, 0.260 mmol) were mixed in 1,4-dioxane (150 mL) under argon, and the mixture was refluxed at 100 °C. After 12 h, the product was extracted with $CHCl_3$ and purified by column chromatography ($CHCl_3$−MeOH, 20:1) to give **7** as a pale yellow powder (1.80 g, 56% yield). Mp: 141−142 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.67 (brs, 2H, H_{m-4}), 7.62 (d, J = 8.6 Hz, 2H, H_{m-3}), 7.49−7.46 (brs, 2H, H_{o-4}), 7.48 (d, J = 8.8 Hz, 2H, H_{o-2}), 7.10 (d, J = 8.6 Hz, 2H, H_{o-3}), 6.95 (d, J = 8.8 Hz, 2H, H_{m-2}). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.0, 155.8, 150.3, 147.4, 133.3, 132.9, 128.5, 121.4, 121.0, 119.1, 116.4. Anal. Calcd for $C_{17}H_{12}OBrN$: C, 62.60; H, 3.71; N, 4.29. Found: C, 62.67; H, 3.83; N, 4.18. IR (KBr, cm^{-1}): 1608, 1596, 1579, 1511, 1477, 1234, 1169, 1010, 844, 808, 591, 556. MS (EI): m/z 325.0 (M^+).

4-[4-(4-Trimethylstannylphenoxy)phenyl]pyridine (8). THF solution (20 mL) of **7** (1.00 g, 3.07 mmol) was added dropwise to a THF (40 mL) solution of *n*-BuLi (2.4 mL, 1.55 M in hexane, 3.70 mmol) at −80 °C under argon, and the mixture was stirred for 1 h. Me_3SnCl (3.7 mL, 1.0 M in THF, 3.70 mmol) was added to the solution at the same temperature. After being stirred for 1 h, the mixture was warmed to room temperature and stirred for 5 h. The product was extracted with $CHCl_3$ and purified by column chromatography ($CHCl_3$−MeOH, 20:1) to give **8** as a white powder (1.05 g, yield 84%). Mp: 85−86 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.63 (d, J = 6.0 Hz, 2H, H_{m-4}), 7.60 (d, J = 8.6 Hz, 2H, H_{m-3}), 7.49 (d, J = 8.4 Hz, 2H, H_{o-2}), 7.46 (d, J = 6.0 Hz, 2H, H_{o-4}), 7.10 (d, J = 8.6 Hz, 2H, H_{o-3}), 7.06 (d, J = 8.4 Hz, 2H, H_{m-2}), 0.30 (s, 9H, −CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.4, 156.8, 150.2,147.5, 137.0, 136.8, 132.7, 128.3, 121.2, 118.9, 118.6, −9.5. IR (KBr, cm^{-1}): 1608, 1576, 1485, 1251, 1224, 1169, 807, 802, 769, 712, 530. Anal. Calcd for $C_{20}H_{21}NOSn$: C, 58.57; H, 5.16; N, 3.42. Found: C, 58.35; H, 5.10; N 3.29. MS (EI): m/z 396 ($M^+ - CH_3$).

Preparation of 2-(*p*-Bromophenyl)-1,10-phenanthroline (9). A 62 mL portion (100 mmol) of a 1.6 M *n*-butyllithium solution in hexane was rapidly added to a degassed solution of *p*-dibromobenzene (26.0 g, 110 mmol) in anhydrous diethyl ether (150 mL) at room temperature and titrated. Then 210 mL (63 mmol) of the 0.3 M *p*-bromophenyllithium solution thus obtained was slowly added, by the means of a double-ended needle, to a degassed suspension of 1,10-phenanthroline monohydrate (4.95 g, 25 mmol) in 180 mL of anhydrous Et_2O kept at 0 °C. After the resulting dark red solution was stirred for 2 h 30 min under argon at 2 °C, it was hydrolyzed with water at 0 °C. The bright yellow Et_2O layer was decanted and the aqueous layer extracted three times with 200 mL portions of CH_2Cl_2. The combined organic layers were thereafter rearomatized by successive additions of MnO_2 under effective magnetic stirring (MnO_2 Merck No. 805958). This reoxidation, easily followed by TLC and the disappearance of the yellow color, was ended after the addition of 73 g of MnO_2. After the mixture was dried over $MgSO_4$, the black slurry could be easily filtered on a sintered

(28) Fujita, M.; Yazaki, J.; Ogura, K. *J. Am. Chem. Soc.* **1990**, *112*, 5645.

glass and the filtrate evaporated to dryness to give 14.9 g of crude **9**, which crystallized upon cooling. This crude solid was filtered over a sintered glass and washed with cold C_6H_6 and subsequently with cold Et_2O, affording 5.93 g (17.7 mmol) of pure **9**. An additional 1.0 g (2.98 mmol) of **9** could be obtained by column chromatography on silica gel (eluent: CH_2Cl_2, 1% MeOH). Overall yield: 82% (6.93 g, 20.68 mmol), colorless solid (mp 187−189 °C). ^{1}H NMR (200 MHz, $CDCl_3$): 9.23 (dd, 1H, H_9, $J_1 = 4.4$ Hz, $J_2 = 1.8$ Hz), 8.29 (d, 1H, H_4, $J = 8.4$ Hz), 8.25 (dd, 1H, H_7, $J_1 = 8.4$ Hz, $J_2 = 1.8$ Hz), 8.22 (d, 1H, H_{o-1}, $J = 8.2$ Hz), 8.04 (d, 1H, H_3, $J = 8.4$ Hz), 7.78 (AB, 2H, $H_{5,6}$, $J = 10.2$ Hz), 7.66 (d, 2H, H_{m-1}, $J = 8.8$ Hz). Anal. Calc for $C_{18}H_{11}N_2Br$: C, 64.50; H, 3.31; N, 8.36. Found: C, 64.75; H, 3.20; N, 8.66. MS (EI): *m*/*z* found 335, calc 335.2.

Preparation of 2,9-Bis(*p*-bromophenyl)-1,10-phenanthroline (10). A 25 mL sample of an etheral solution of *p*-bromophenyllithium (prepared as above from 2.9 g, 12 mmol of *p*-dibromobenzenze, and 11 mmol of *n*-Buli) was slowly added, by means of a double-ended needle, to a degassed suspension of **9** (2.01 g, 6 mmol) in 70 mL of anhydrous Et_2O maintained at 2 °C. The resulting dark purple solution was stirred during three further hours at 3 °C. After hydrolysis at 0 °C, decantation, three extractions with CH_2Cl_2, and rearomatization with 8.0 g of MnO_2, 3.05 g of a crude mixture was obtained as a pale yellow solid. Column chromatography of the latter over silica gel (eluent: CH_2Cl_2, 0.5% MeOH) afforded pure **10** (2.6 g, 5.30 mmol, 88% yield) as a colorless solid (mp 219−221°C). ^{1}H NMR (200 MHz, $CDCl_3$): 8.33 (d, 4H, H_{o-1}, $J = 8.8$ Hz), 8.33 (d, 2H, $H_{4,7}$, $J = 8.8$ Hz), 8.12 (d, 2H, $H_{3,8}$, $J = 8.4$ Hz), 7.81 (s, 2H, $H_{5,6}$), 7.73 (d, 4H, H_{m-1}, $J = 8.8$ Hz). Anal. Calc for $C_{24}H_{14}N_2Br_2$: C, 58.81; H, 2.88; N, 5.71. Found: C, 59.04; H, 2.79; N, 5.74. MS (EI): *m*/*z* found 490, calc 490.2.

2,9-Bis[4′-(4-pyridyl-4-phenoxy)biphenyl]-1,10-phenanthroline (1b). Compound **8** (400 mg, 0.98 mmol), LiCl (170 mg, 4.00 mmol), and $[PdCl_2(PPh_3)_2]$ (30 mg, 0.04 mmol) were combined in toluene (50 mL) under argon. 2,9-Bis(4-bromophenyl)-1,10-phenanthroline (**10**, 196 mg, 0.40 mmol) in toluene (30 mL) was added to the mixture, and the mixture was stirred at 120 °C. After 12 h, the product was extracted with $CHCl_3$ and purified by column chromatography ($CHCl_3$−MeOH, 20:1) to give **1b** as colorless crystals (150 mg, yield 45%). Mp: 249−250 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.66 (d, $J = 6.1$ Hz, 4H, H_{m-4}), 8.59 (d, $J = 8.3$ Hz, 4H, H_{o-1}), 8.35 (d, $J = 8.3$ Hz, 2H, $H_{4,7}$), 8.22 (d, $J = 8.3$ Hz, 2H, $H_{3,8}$), 7.84 (d, $J = 8.3$ Hz, 4H, H_{m-1}), 7.83 (s, 2H, $H_{5,6}$), 7.75 (d, $J = 8.4$ Hz, 4H, H_{o-2}), 7.65 (d, $J = 8.7$ Hz, 4H, H_{m-3}), 7.50 (d, $J = 6.1$ Hz, 4H, H_{o-4}), 7.19 (d, $J = 8.7$ Hz, 4H, H_{o-3}), 7.18 (d, $J = 8.4$ Hz, 4H, H_{m-2}). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.3, 154.2, 153.9, 147.3, 146.0, 143.7, 139.0, 135.9, 134.9, 134.1, 130.2, 126.3, 126.2, 125.9, 125.8, 125.0, 123.8, 119.3, 118.0, 117.5, 116.8. IR (KBr, cm^{-1}): 1596, 1506, 1484, 1245, 835, 818, 798, 418. Anal. Calcd for $C_{58}H_{38}O_2N_4 \cdot H_2O$: C, 82.84; H, 4.74; N, 6.66. Found: C, 82.86; H, 4.68; N, 6.57.

4-Bromo-4′-iododiphenyl Ether (12). 4-Bromodiphenyl ether (**11**, 5 g, 20 mmol) was stirred in 100 mL of acetic acid. ICl (4.9 g, 30 mmol) in 30 mL of acetic acid was added dropwise to the solution at room temperature. When the addition was over, the solution was heated at reflux for 2 h. The acetic acid was then evaporated. The solid was taken up in CH_2Cl_2. The solution was decolorized with 10% $Na_2S_2O_3$, and Na_2CO_3 was added until pH = 7. The organic layer was also washed with water. After extracting with CH_2Cl_2, drying over $MgSO_4$, evaporating the solvent, and recrystallizing in hexane, the product was obtained as a white solid (7.3 g, yield 99%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.63 (d, $J = 9.0$ Hz, 2H), 7.45 (d, $J = 8.8$ Hz, 2H), 6.88 (d, $J = 9.0$ Hz, 2H), 6.88 (d, $J = 8.8$ Hz, 2H).

4-Bromo-4′-diphenyl Ether Boronic Ester (13). A solution of 1.58 g of **12** (4.22 mmol) in 70 mL of diethyl ether was degassed and cooled to −78 °C. Then, 0.63 mL of TMEDA (4.22 mmol) were added, followed by 2.7 mL of *n*-butyllithium in hexane (4.64 mmol). After stirring for 3 h at −78 °C, a degassed solution of trimethylborate (1.68 g, 17 mmol) in 15 mL of dry Et_2O was added via cannula. The reaction was stirred overnight and then allowed to warm to room temperature before hydrolysis with 100 mL of a 4 M HCl solution. The two layers were separated, and ether was evaporated. The solid was taken up in 100 mL of aqueous Na_2CO_3 (2 M) and 100 mL of Et_2O. The two layers were separated again. The aqueous layer was acidified and extracted three times with 100 mL of Et_2O. The combined organic layers were dried over $MgSO_4$ to yield the free acid boronic derivative as a white solid (0.86 g). This solid was dissolved in 30 mL of benzene with 0.31 g of 2,2-dimethyl-1,3-propanediol (1 equiv) and a catalytic amount of *p*-toluenesulfonic acid. This mixture was heated under reflux for 2 h. Evaporation of the solvent gave **13** as a white solid (1.06 g, 70% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.78 (d, $J = 8.4$ Hz, 2H), 7.44 (d, $J = 9.1$ Hz, 2H), 6.96 (d, $J = 9.1$ Hz, 2H), 6.91 (d, $J = 8.4$ Hz, 2H), 3.77 (s, 4H), 1.03 (s, 6H). ^{13}C NMR (200 MHz, $CDCl_3$): δ 156.1, 153.0, 135.7, 132.7, 129.7, 120.8, 117.8, 116.0, 72.3, 31.9, 21.9. Anal. Calcd for $C_{17}H_{18}O_3BBr$: C, 56.55; H, 5.03. Found: C, 56.50; H, 4.93. MS (EI): *m*/*z* 360.1 (M^+).

Compound 7. To a degassed solution of 4-bromopyridine hydrochloride (**14**, 0.65 g, 3.36 mmol) and $[Pd(PPh_3)_4]$ (110 mg, 0.17 mmol) in 80 mL of toluene were added 30 mL of a degassed solution of 2 M aqueous Na_2CO_3 and a solution of **13** (1.21 g, 3.36 mmol) in 20 mL of toluene under argon. It is very important to respect the following sequence in the additions: (1) 4-iodopyridine in toluene, (2) vacuum/Ar three times, (3) addition of the catalyst, (4) vacuum/Ar three times, (5) addition of the degassed solution of Na_2CO_3, (6) addition of the degassed solution of the boronic ester. After 2 h of reflux, the reaction mixture was allowed to cool to room temperature. The solvent was evaporated, and the crude product was chromatographed over alumina using hexane−dichloromethane as the eluents. Compound **7** was obtained (CH_2Cl_2) as a white solid (0.92 g, 80% yield).

4-Boronic Ester-4′-pyridyldiphenyl Ether (16). Bis-pinacolato diboron (**15**, 0.63 g, 2.48 mmol), **7** (0.74 g, 2.26 mmol), KOAc (0.67 g, 6.78 mmol), and $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (55 mg, 0.07 mmol) were dissolved in freshly distilled dioxane (15 mL). The mixture was stirred under argon at 80 °C for 14 h. After the solution had cooled to room temperature, 20 mL of water was added. The dioxane was evaporated under vacuum, and 100 mL of CH_2Cl_2 was added. The organic layer was dried over $MgSO_4$, filtered, and evaporated. The crude was then purified on a short silica column to give a black oil (yield 95%). The ^{1}H NMR was very nice, and the product was used without other purification. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.65 (d, $J = 6.2$ Hz, 2H), 7.83 (d, $J =$ 8,6 Hz, 2H), 7.62 (d, $J = 8.6$ Hz, 2H), 7,49 (d, $J = 6.2$ Hz, 2H), 7.12 (d, $J = 8.6$ Hz, 2H), 7.05 (d, $J = 8.6$ Hz, 2H), 1.36 (s, 12H).

Ligand 1b. To a degassed solution of 2,9-bis(4-bromophenyl)-1,10-phenanthroline **10** (0.45 g, 0.91 mmol) and $[Pd(PPh_3)_4]$ (84 mg, 0.07 mmol) in 30 mL of toluene were added 9 mL of a degassed solution of 2 M aqueous Na_2CO_3 and a solution of **16** (0.75 g, 2.00 mmol) in 10 mL of toluene under argon. After 17 h of reflux, the reaction mixture was allowed to cool to room temperature and a precipitate appeared. It was filtered off and washed with water, toluene, and ether to yield 0.60 g of the ligand **1b** (yield 80%).

$[Cu(1b)_2]\cdot PF_6$ (17b). Ligand **1b** (33.0 mg, 0.04 mmol) and $Cu(CH_3CN)_4 \cdot PF_6$ (7.5 mg, 0.02 mmol) were combined in DMF (1 mL) at room temperature under argon. The mixture was stirred for 15 min to give a clear dark red solution. Cu(I) complex **17b** was precipitated as a purple powder by adding a large amount of diethyl ether. Yield: 93%. Mp: 191−192 °C dec. ^{1}H NMR (500 MHz, DMF-d_7): δ 9.27 (d, $J = 8.4$ Hz, 4H, $H_{4,7}$), 8.66 (d, $J = 8.4$ Hz, 4H, $H_{3,8}$), 8.62 (s, 4H, $H_{5,6}$), 8.48 (d, $J = 8.0$ Hz, 8H, H_{m-3}), 8.26 (d, $J = 7.7$ Hz, 8H, H_{o-1}), 7.86 (d, $J = 8.2$ Hz, 8H, H_{o-2}), 7.73 (d, $J = 8.0$ Hz, 8H, H_{o-3}), 7.69 (d, $J = 8.2$ Hz, 8H, H_{m-2}), 7.46 (d, $J = 7.7$ Hz, 8H, H_{m-1}). ^{13}C NMR (125 MHz, DMF-d_7): δ 158.7 (*C*q), 157.1 (*C*q), 156.7 (*C*q), 144.1 (*C*q), 140.9 (*C*q), 138.44 (*C*$H_{4,7}$), 138.39 (*C*q), 135.7 (*C*q), 129.4 (*C*H_{o-1}), 129.2 (*C*H_{o-2}), 129.1 (*C*H_{m-3}), 127.2 (*C*$H_{5,6}$), 126.0 (*C*H_{m-1}), 125.3 (*C*$H_{3,8}$),

120.0 (CH_{o-3}), 119.9 (CH_{m-2}). IR (KBr, cm^{-1}): 1597, 1485, 1244, 1174, 842, 557. CSI-MS *m*/*z* 1708.04 [**17b** − PF_6]$^+$.

[Cu(enPd)$_2$(1b)$_2$]·PF$_6$·(NO$_3$)$_4$ (18b). Cu(I) complex **17b** (18.5 mg, 0.01 mmol) and (en)Pd(NO_3)$_2$ (5.8 mg, 0.02 mmol) were combined in DMF (1 mL) at room temperature, and the mixture was stirred for 30 min. The solution color was slightly changed to reddish brown from dark red. Cu(I)Pd(II) complex **18b** was precipitated as a reddish purple powder by adding a large amount of diethyl ether, and it was recrystallized from DMF−MeOH−diethyl ether as deep red microcrystals. Yield: 92%. Mp > 300 °C. ^{1}H NMR (500 MHz, DMF-d_7): δ 9.64 (d, J = 6.3 Hz, 8H, H_{m-4}), 9.14 (d, J = 8.3 Hz, 4H, $H_{4,7}$), 8.73 (d, J = 6.3 Hz, 8H, H_{o-4}), 8.70 (d, J = 8.6 Hz, 2H, H_{m-3}), 8.61 (d, J = 8.3 Hz, 4H, $H_{3,8}$), 8.49 (s, 4H, $H_{5,6}$), 8.25 (d, J = 8.0 Hz, 8H, H_{o-1}), 7.89 (d, J = 8.6 Hz, 8H, H_{o-3}), 7.60−7.55 (d, 16H, H_{m-2} and H_{o-2}), 7.32 (d, J = 8.0 Hz, 8H, H_{m-1}), 3.57 (brs, 8H, *H-en*). ^{13}C NMR (125 MHz, DMF-d_7): δ 159.5 (*C*q), 158.3 (*C*q), 156.4 (*C*q), 152.9 (CH_a), 150.7 (*C*q), 143.9 (*C*q), 140.9 (*C*q), 138.4 (*C*q), 138.3 ($CH_{4,7}$), 135.0 (*C*q), 131.4 (*C*q), 130.2 (CH_{m-3}), 129.6 (CH_{o-1}), 129.1 (*C*q), 128.9 (CH_{m-2} or CH_{o-2}), 127.1 ($CH_{5,6}$), 125.6 (CH_{m-1}), 124.7 ($CH_{3,8}$), 123.8 (CH_b), 121.8 (CH_{o-3}), 118.7 (CH_{m-2} or CH_{o-2}), 48.0 (CH_2). IR (KBr, cm^{-1}): 1596, 1486, 1385, 1246, 1174, 841, 557. CSI-MS: *m*/*z* 546.5 [(**18b** − PF_6 − $(NO_3)_3$) + $(MeCN)_2$]$^{4+}$, 721.6 [(**18b** − PF_6 − $(NO_3)_2$)]$^{3+}$.

[Cu(1a)$_2$]·PF$_6$ (17a) and [Cu(enPd)$_2$(1a)$_2$]·PF$_6$·(NO$_3$)$_4$ (18a). Ligand **1a** (9.9 mg, 0.010 mmol) and Cu(CH_3CN)$_4$·PF_6 (1.9 mg, 0.005 mmol) were combined in CH_3CN−DMF (1:1, 1 mL) at room temperature. The mixture was stirred for 15 min to give a clear dark red solution. In a control experiment using CD_3CN−DMF-d_7 (1:1), the exclusive formation of **16a** was confirmed by NMR. To the dark red solution of **17a** was added (en)Pd(NO_3)$_2$ (2.9 mg, 0.010 mmol), and the reaction mixture was stirred for 1 h at room temperature. From the red reaction solution, **18a** was isolated as red microcrystals by adding a large amount of diethyl ether (12.5 mg, 85%). Physical properties of **17a**: ^{1}H NMR (500 MHz, CD_3CN−DMF-d_7): δ 8.91 (s, 4H, $H_{5,6}$), 8.53 (d, J = 8.8 Hz, 8H, H_{o-2}), 8.52 (s, 4H, $H_{3,8}$), 8.36 (d, J = 8.3 Hz, 8H, H_{m-1}), 7.87 (d, J = 8.5 Hz, 8H, H_{m-3}), 7.86 (d, J = 8.8 Hz, 8H, H_{m-2}), 7.80 (d, J = 8.5 Hz, 8H, H_{o-3}), 7.50 (d, J = 8.3 Hz, 8H, H_{o-1}), 3.79 and 2.33−1.93 (m, 40H, −CH_2−), 1.53 (t, J = 6.5 and 7.0 Hz, 12H, −CH_3). CSI-MS data for **17a** were obtained by analyzing the CH_3CN−DMF (1:1) solution of **17a** (5 mM), which was prepared independently: *m*/*z* 2046.2, [**17a** − PF_6]$^+$. Physical properties of **18a**: ^{1}H NMR (500 MHz, CD_3CN−DMF-d_7): δ 9.67 (d, J = 6.8 Hz, 8H, H_{m-4}), 8.72 (d, J = 8.8 Hz, 8H, H_{o-2}), 8.70 (s, 4H, $H_{5,6}$), 8.69 (d, J = 6.8 Hz, 8H, H_{o-3}), 8.48 (s, 4H, $H_{3,8}$), 8.32 (d, J = 8.0 Hz, 8H, H_{m-1}), 7.97 (d, J = 8.8 Hz, 8H, H_{m-2}), 7.40 (d, J = 8.0 Hz, 8H, H_{o-1}), 6.49 (brs, 8H), 3.64 and 2.24−1.83 (m, 40H, −CH_2−), 1.46 (t, J = 6.5 and 7.5 Hz, 12H, −CH_3). CSI-MS data for **18a** was obtained by analyzing the CH_3CN−DMF (1:1) solution of **18a** (0.25 mM), which was prepared independently: *m*/*z* 548.8 [(**18a** − PF_6 − $(NO_3)_4$) + $(dmf)_5$]$^{5+}$, 646.7 [(**18a** − PF_6 − $(NO_3)_3$) + $(dmf)_2$]$^{4+}$, 834.5 [**18a** − PF_6 − $(NO_3)_2$]$^{3+}$. CSI−HRMS: calcd for [(**18a** − PF_6 − $(NO_3)_4$) + $(dmf)_5$]$^{5+}$ *m*/*z* 548.8238; found 548.8193.

[Cu(1b)(2)]·PF$_6$ (19). Ligand **1b** (33.0 mg, 0.04 mmol), m-30 **2**[28] (22.6 mg, 0.04 mmol), and $CuPF_6$·4CH_3CN (15.0 mg, 0.04 mmol) were combined in DMF (2 mL) at room temperature under argon. The mixture was stirred for 15 min to give a clear dark red solution. Cu complex **19** was isolated as a purple powder by adding a large amount of diethyl ether. Yield: 95%. Mp: 163−164 °C dec. ^{1}H NMR (500 MHz, DMF-d_7): δ 9.43 (d, J = 8.3 Hz, 2H, $H_{4,7}$), 9.19 (d, J = 8.3 Hz, 2H, $H_{4',7'}$), 8.96 (s, 2H, $H_{5,6}$), 8.73 (d, J = 8.3 Hz, 2H, $H_{3,8}$), 8.59 (s, 2H, $H_{5',6'}$), 8.53 (d, J = 8.3 Hz, 2H, $H_{3',8'}$), 8.47 (d, J = 7.9 Hz, 4H, H_{m-3}), 8.29 (d, J = 8.0 Hz, 4H, H_{o-1}), 7.99 (d, J = 8.4 Hz, 4H, $H_{o'}$), 7.88 (d, J = 8.4 Hz, 4H, H_{o-2}), 7.74 (d, J = 7.9 Hz, 4H, H_{o-3}), 7.69 (d, J = 8.4 Hz, 4H, H_{m-2}), 7.45 (d, J = 8.0 Hz, 4H, H_{m-1}), 6.67 (d, J = 8.4 Hz, 4H, $H_{m'}$), 4.38−4.15 (brs, 20H, CH_2). ^{13}C NMR (125 MHz, DMF-d_7): δ 159.6 (*C*q), 158.7 (*C*q), 157.10 (*C*q), 157.05 (*C*q), 156.2 (*C*q), 143.9 (*C*q), 140.8 (*C*q), 138.9 ($CH_{4,7}$), 138.4 (*C*q), 137.9 ($CH_{4',7'}$), 135.7 (*C*q), 132.9 (*C*q), 130.1 ($CH_{o'}$), 129.4 (CH_{o-1}), 129.14 (CH_{m-3}), 129.06 (CH_{o-2}), 128.7 (*C*q), 128.1 ($CH_{5,6}$), 126.8 ($CH_{5',6'}$), 125.8 (CH_{m-1}), 125.1 ($CH_{3,8}$), 124.6 ($CH_{3',8'}$), 120.0 (CH_{m-2}), 119.9 (CH_{o-3}), 113.6 ($CH_{m'}$), 71.5, 71.0, 69.1, 67.4, 65.8 15.4 (CH_2). IR (KBr, cm^{-1}): 1596, 1486, 1245, 1175, 1108, 841,557. CSI-MS *m*/*z* 1451.86 [**19** − PF_6]$^+$.

[Cu(enPd)(1b)(2)]·PF$_6$·(NO$_3$)$_2$ (20). This complex was obtained as a brown powder by the reaction of (en)Pd(NO_3)$_2$ (2.9 mg, 0.01 mmol) with **19** (16.6 mg, 0.01 mmol) in DMF (1 mL) in a manner similar to that of **18b**. Yield: 85%. Mp: 262−263 °C dec. ^{1}H NMR (500 MHz, DMF-d_7): δ 9.61 (d, J = 6.6 Hz, 4H, H_{m-4}), 9.43 (d, J = 8.3 Hz, 2H, $H_{4,7}$), 9.02 (d, J = 8.3 Hz, 2H, $H_{4',7'}$), 8.97 (s, 2H, $H_{5,6}$), 8.74 (d, J = 8.3 Hz, 2H, $H_{3,8}$), 8.70 (d, J = 6.6 Hz, 4H, H_{o-4}), 8.67 (d, J = 8.7 Hz, 4H, H_{m-3}), 8.43 (d, J = 8.3 Hz, 2H, $H_{3',8'}$), 8.38 (s, 2H, $H_{5',6'}$), 8.28 (d, J = 8.1 Hz, 4H, H_{o-1}), 7.98 (d, J = 8.5 Hz, 4H, $H_{o'}$), 7.86 (d, J = 8.7 Hz, 4H, H_{o-3}), 7.62 (d, J = 8.6 Hz, 4H, H_{o-2}), 7.54 (d, J = 8.6 Hz, 4H, H_{m-2}), 7.31 (d, J = 8.1 Hz, 4H, H_{m-1}), 6.62 (d, J = 8.5 Hz, 4H, $H_{m'}$), 4.36−4.13 (brs, 20H, CH_2), 3.56 (brs, 4H, en). ^{13}C NMR (125 MHz, DMF-d_7): δ 159.7 (*C*q), 159.5 (*C*q), 158.2 (*C*q), 156.9 (*C*q), 155.9 (*C*q), 152.9 (CH_a), 150.7 (*C*q), 143.8 (*C*q), 143.7 (*C*q), 140.6 (*C*q), 138.8 ($CH_{4,7}$), 138.6 (*C*q), 137.8 ($CH_{4',7'}$), 135.1 (*C*q), 132.5 (*C*q), 131.3 (*C*q), 130.3 ($CH_{o'}$), 130.2 (CH_{m-3}), 129.5 (CH_{o-1}), 129.3 (*C*q), 128.9 (CH_{o-2}), 128.5 (*C*q), 128.1 ($CH_{5,6}$), 126.6 ($CH_{5',6'}$), 125.5 (CH_{m-1}), 124.5 ($CH_{3,8}$), 124.4 ($CH_{3',8'}$), 123.8 (CH_b), 121.7 (CH_{o-3}), 118.8 (CH_{m-2}), 113.4 ($CH_{m'}$), 71.5, 71.0, 70.9, 69.0, 67.3, 65.8, 48.0 (CH_2). IR (KBr, cm^{-1}): 1596, 1487, 1384, 1247, 1176, 842, 557. CSI-HRMS: calcd for [(**20** − PF_6 − $(NO_3)_2$) + $(dmf)_2$]$^{3+}$ *m*/*z* 588.5172; found 588.5159.

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