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Coordination Chemistry-Assembled Porphyrinic Catenanes

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Abstract: Non covalent [2]catenanes were synthesized in high yield as kinetic products or as thermodynamic products after completion of an equilibrium. These sophisticated architectures were assembled in two steps, from an oblique bis-zinc(II) porphyrin and two different dipyridyl chelates, by using Cu(I)−N interactions to assemble acyclic complexes and Zn(II)−N interactions to generate rings. ^{1}H NMR including 2D COSY and ROESY experiments were used to characterize each compound. Spectrophotometric titrations highlight the influence of geometry in terms of distances and angles in non covalent coordinated assemblies. In fact, it was proved that a perfect fit leads to highly stable coordination chemistry-assembled species.

Introduction

Topologically nontrivial molecules such as catenanes and knots, as well as their parent compounds, the rotaxanes, continue to attract much attention.[1] Originally, these compounds used to represent mostly synthetic challenges. Nowadays, they are also made and investigated in relation to controlled dynamic species ("molecular machines"),[2] electron and energy transfer processes,[3] or novel materials.[4] Whereas the preparation of catenanes synthesized by forming stable covalent bonds in the last ring-forming step is much documented, the formation of such compounds under thermodynamic control, either using labile covalent bonds such as, for example, imines[5] or noncovalent bonds (mostly hydrogen or coordination bonds), is much less common. A few remarkable examples of such systems, assembled via formation of hydrogen bonds, have been reported in recent years.[6] In the field of transition-metal-incorporating catenanes for which the ring-forming step involves the formation of a coordination bond, the pioneering work of Fujita and his co-workers is particularly significant.[7] Our group has also been interested in closing the constitutive catenane rings or attaching the rotaxane stoppers by forming transition metal−ligand bonds. By combining copper(I)−1,10-phenanthroline interactions and palladium(II)−pyridine interactions, several catenanes assembled via coordination chemistry have been made in collaborative work with Fujita and his group, thus demonstrating the power of the approach utilizing two distinct coordination bonds. The reactions were performed under thermodynamic control.[7a,d−f]

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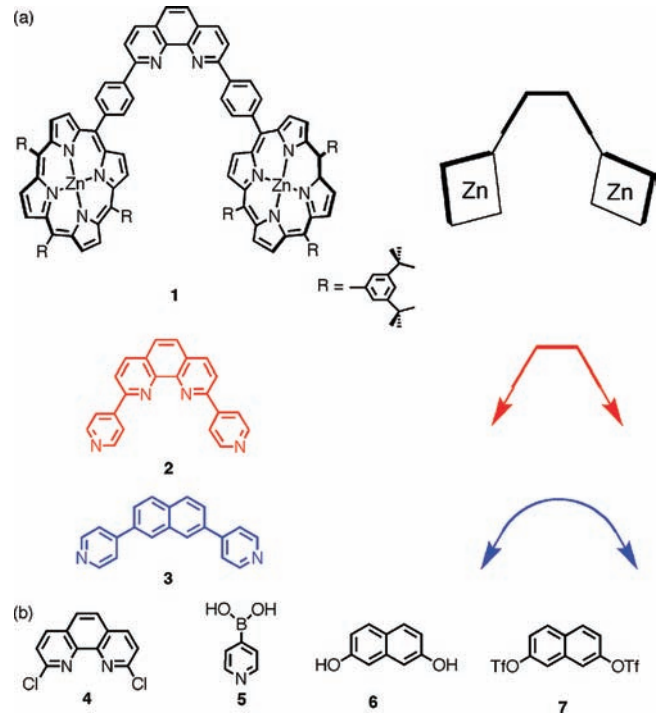
In other work, the metal used in the final step was ruthenium(II), implying that the compounds were obtained as kinetic products, rather than thermodynamic products.[8] Porphyrin-incorporating catenanes and rotaxanes represent a particularly promising family of compounds. The synthesis of such molecules and some of their photochemical properties have recently been reviewed.[3g,j] It is indeed particularly interesting to construct such compounds under thermodynamic control using coordination bonds only in the final assembly step once the organic fragments had been synthesized.[9,6] We now report that when the copper(I)−1,10-phenanthroline based strategy is used in association with the coordination bond formed between a pyridyl group and the central zinc(II) atom of a porphyrin, [2]catenanes can also be obtained, essentially in a quantitative way. A preliminary account of the work has recently been published.[10] In the present report, we will generalize the concept and use two geometrically very different peripheral fragments to show that the thermodynamics of formation of the coordination bond assembled porphyrinic catenanes can be governed by playing with the geometry of the various organic fragments used. In particular, remarkably stable edifices can be obtained if the geometry is optimized and if the component can assemble in such a way that the pyridine fragments are coordinated to the zinc(II) atoms in an axial fashion, the pyridyl group being orthogonal to the porphyrin plane.

Scheme 1. (a) Chemical Structures of **1**−**3** and Their Schematic Representations.[a] (b) Chemical Structures of the Precursors Used for the Synthesis of **2** and **3**



[a] The porphyrin units are represented as lozenges. The 1,10-phenanthroline connectors are indicated by an U-shaped symbol. An arc of a circle symbol represents the naphthalene unit. Each 4-pyridyl nucleus is indicated by an arrow.

Results and Discussion

1. Synthesis of the Ligands. The chemical structure of the various ligands used to assemble porphyrinic [2]catenanes, their schematic representations, and various precursors used in their synthesis are depicted in Scheme 1. The synthesis of bisporphyrin **1** was described long ago and used a low-yielding procedure.[11] Recently, two new routes to **1** based on C−C

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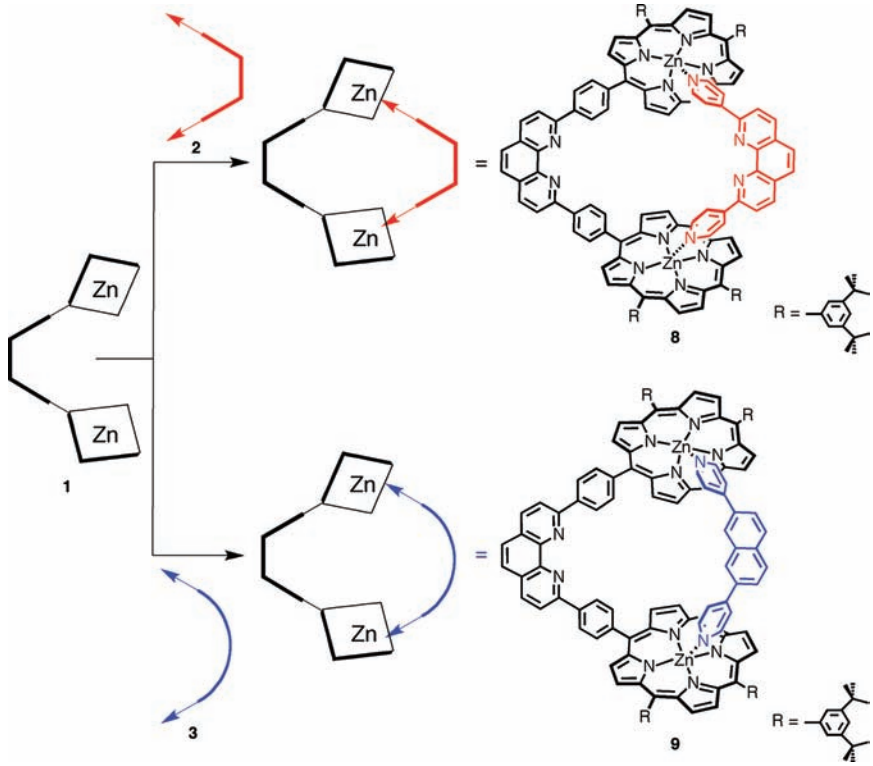
Scheme 2. Principle of Formation of Noncovalently Assembled Rings: Schematic Representation and Chemical Structures of **8** and **9**



coupling reactions and allowing more efficient yields were reported.[12] Both dipyridyl-incorporating chelates **2** and **3** were obtained thanks to a double-Suzuki cross-coupling reaction. Compound **2** was obtained from 2,9-dichloro-1,10-phenanthroline **4** and the commercially available pyridine-4-boronic acid **5**. Phenanthroline **4** was prepared on a gram scale in three steps from 1,10-phenanthroline monohydrate as already described.[13] The synthesis of **3** is also based on a double Suzuki cross-coupling reaction involving **5** and bis-triflate naphthalene derivative **7**. Compound **7** could also be obtained on a gram scale by converting the two hydroxy groups of the commercially available 2,7-dihydroxynaphthalene **6** to triflate functions.

2. Noncovalently Assembled Rings and [2]Catenanes. The strength of the association between **1** and **2** or between **1** and **3** in the macrocyclic structures, which will be the constitutive rings of the catenanes, was first tested. The principle is shown is Scheme 2.

Compounds **1** and **2** were used in stoichiometric amounts, dissolved in degassed CH_2Cl_2 ($c = 4.5 \times 10^{-3}$ M for each compound), and the resulting solution was stirred at room temperature under argon for 3 h. After removal of the solvent, **8** was obtained quantitatively. Ring **8** was characterized by ^{1}H NMR including COSY and ROESY. Upon complexation, the pyridine protons of **2** undergo an expected strong upfield shift. Their signals are also broad due to restricted motions of the pyridine nuclei as already observed in similar systems where the same bis-porphyrin **1** is coordinated to cis(4-pyridyl)porphyrins.[14,15] Compound **9** was obtained using the same procedure by mixing stoichiometric amounts of **1** and **3**. The same observations about the signals of the pyridinic protons were made. By combining Cu(I)−N interactions to assemble acyclic complexes and Zn−N interactions to generate rings, formation of [2]catenanes can be envisaged. The principle is depicted in Scheme 3.

The chemical structures of the various entwined precursors $\mathbf{10}^+$ and $\mathbf{11}^+$ as well as the final catenanes that can be obtained ($\mathbf{12}^+$, $\mathbf{13}^+$, $\mathbf{14}^+$, and $\mathbf{15}^+$) are represented in Scheme 4.

To form the entwined precursor $\mathbf{10}^+$, a solution of $Cu(CH_3CN)_4 \cdot PF_6$ (1.05 equiv) in CH_3CN was added to a solution of **1** (2 equiv) in CH_2Cl_2. After the mixture was stirred at room temperature under argon for 3 h, the solvents were removed under reduced pressure, leading quantitatively to complex $\mathbf{10 \cdot PF_6}$ as a purple solid. $\mathbf{10 \cdot PF_6}$ was characterized by ^{1}H NMR and ES-MS. The complex $\mathbf{11 \cdot PF_6}$ was obtained in a similar way as a deep red solid by mixing a solution of $Cu(CH_3CN)_4 \cdot PF_6$ (1.05 equiv) in CH_3CN with a solution of **2** (2 equiv) in CH_2Cl_2. $\mathbf{11 \cdot PF_6}$ was not obtained quantitatively but in 85% yield as washing of the solid with water was necessary to remove an unidentified impurity. $\mathbf{11 \cdot PF_6}$ was also characterized by ^{1}H NMR and ES-MS.

$\mathbf{10 \cdot PF_6}$ and $\mathbf{11 \cdot PF_6}$ were then reacted with their complementary ligands **2** and **1**, respectively. The formation of [2]catenanes $\mathbf{12 \cdot PF_6}$, $\mathbf{13 \cdot PF_6}$, and $\mathbf{14 \cdot PF_6}$ was expected in both cases.

Compound $\mathbf{10 \cdot PF_6}$ was reacted with 2 equiv of **2**. The two components were mixed in a degassed solution of CH_2Cl_2. After 3 h, the solvent was pumped off, and ^{1}H NMR showed the formation of catenane $\mathbf{12 \cdot PF_6}$ as sole product of the reaction.[10] In order to check whether $\mathbf{12}^+$ is obtained as a kinetic product or if it is formed under thermodynamic control, two types of experiments were carried out, as described below.

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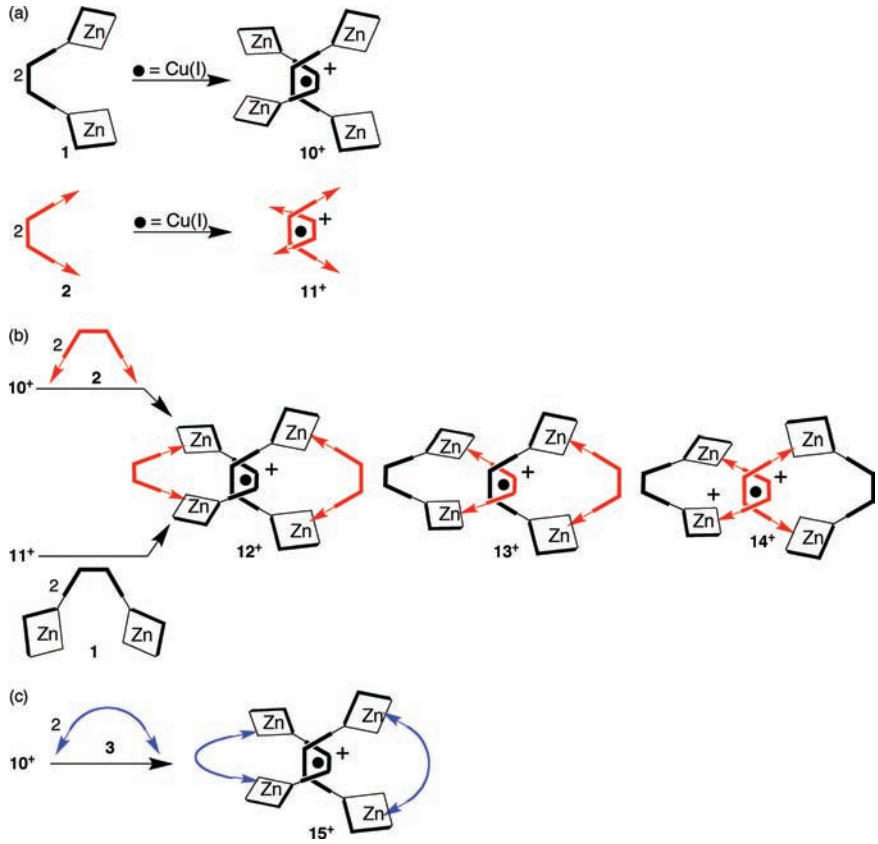
Scheme 3. Stepwise Formation of [2]Catenanes Using Coordination Bonds Only: (a) Formation of Copper(I) Precursors $\mathbf{10}^+$ and $\mathbf{11}^+$; (b) Formation of [2]Catenanes by Four Zn(II)−N Interactions between the Intertwined Precursors and the Complementary Ligand;[a] (c) Unambiguous Formation of $\mathbf{15}^+$ as Sole Catenane from $\mathbf{10}^+$ and **3**



[a] Reacting $\mathbf{10}^+$ with **2** or $\mathbf{11}^+$ with **1** should lead to the same mixture of catenanes $\mathbf{12}^+$, $\mathbf{13}^+$, and $\mathbf{14}^+$ provided the reaction is carried out under thermodynamic control.

$\mathbf{12}^+$ was dissolved in CD_2Cl_2. The solution was monitored by ^{1}H NMR as a function of time. After one night at room temperature, new peaks appeared which correspond to the presence of the asymmetric catenane $\mathbf{13}^+$. The relative proportion of $\mathbf{12}^+$ and $\mathbf{13}^+$ could be estimated as 80% of $\mathbf{12}^+$and 20% of $\mathbf{13}^+$. This proportion did not change even after 2 weeks. The ^{1}H NMR spectrum of $\mathbf{12}^+$, obtained after 3 h, and that of the mixture of $\mathbf{12}^+$ and $\mathbf{13}^+$, obtained after one night, are shown in Figure 1.

In the second experiment, $Cu(CH_3CN)_4\cdot PF_6$ in CH_3CN was added to a CH_2Cl_2 solution of **1** and **2** (Cu^I/**1**/**2**: 1:2:2). After one day at room temperature with stirring under argon, ^{1}H NMR showed that the same relative proportion of $\mathbf{12}^+$ and $\mathbf{13}^+$ as in the previous experiment (approximately 80%: 20% respectively) was obtained.

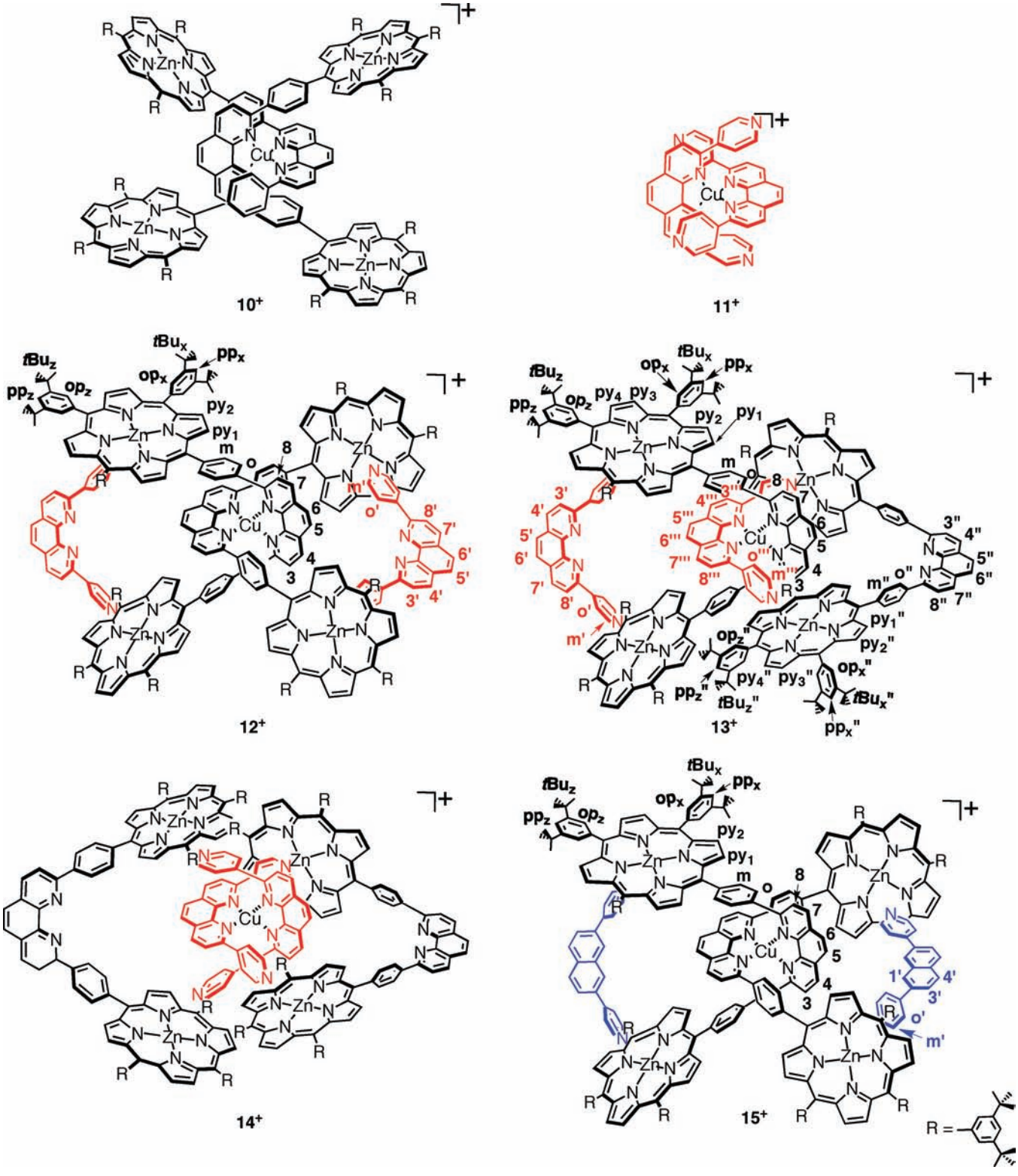
From these two experiments it is clear that $\mathbf{12}^+$ is the kinetic product while the thermodynamic equilibrium is a 80/20 mixture of $\mathbf{12}^+$ and $\mathbf{13}^+$, respectively. These experiments also showed that $\mathbf{12}^+$ is the major and thus the most stable compound. So far, catenane $\mathbf{14}^+$ could not be detected.

The greater stability of $\mathbf{12}^+$ versus $\mathbf{13}^+$ can be relatively easily explained by considering the pyridyl−Zn interaction. The magnitude of the interaction is mostly determined by the basicity of the donor ligand and the Lewis acidity of the Zn atom. The more basic the ligand and the more acidic the central zinc atom, the stronger the interaction. Coordination of **1** to the central copper(I) atom in $\mathbf{12}^+$ increases the Zn acidity and thus favors formation of $\mathbf{12}^+$ over that of $\mathbf{13}^+$. In this compound, two pyridinic groups, respectively, would be made less basic than in free **2**. This effect is detrimental to the formation of $\mathbf{13}^+$. The formation of $\mathbf{14}^+$ is excluded for steric reasons; in the central core constituted by complex $\mathbf{11}^+$, the distance between the four pyridyl groups is too small and the porphyrins too bulky to coordinate four of them perpendicularly to the pyridyl group. To confirm this hypothesis, $\mathbf{11}\cdot\mathbf{PF_6}$ (1 equiv) was mixed with **1** (2 equiv) in CH_2Cl_2. The mixture was allowed to react overnight at room temperature under argon. The solvent was removed under reduced pressure. NMR studies showed the quantitative formation of the asymmetric catenane $\mathbf{13}\cdot\mathbf{PF_6}$ (Figure 1). The compound was dissolved in CD_2Cl_2 and the solution was monitored by ^{1}H NMR. After 2 weeks, a ratio of 65% of $\mathbf{12}^+$ and 35% of $\mathbf{13}^+$ was reached, and it did not change. In this case, $\mathbf{13}^+$ is the kinetic product of the reaction, whereas the mixture of $\mathbf{12}^+$ and $\mathbf{13}^+$represents the thermodynamic equilibrium. Compound $\mathbf{12}^+$ is the major compound, proving once more that it is the most stable compound according to the pyridyl−Zn interactions.

Finally, complex $\mathbf{10}\cdot\mathbf{PF_6}$ was reacted with 2 equiv of **3**. This time, only one species is expected because **3** has no coordination sites for copper(I). Experimentally, the two components were mixed in stoichiometric amounts in a degassed solution of CH_2Cl_2. After 1 h, the solvent was removed, and ^{1}H NMR proved the quantitative formation of the catenane $\mathbf{15}\cdot\mathbf{PF_6}$. Figure 2 shows the NMR spectrum of $\mathbf{15}^+$.

3. Association Constant. In order to evaluate the stability of the various rings and [2]catenanes, UV−vis titrations were carried out. A solution of bis-zinc derivative (**1** or $\mathbf{10}^+$) in toluene ($c \approx 10^{-6}$ M) was prepared. In this solution, constant

Scheme 4. Chemical Structures of the Interlocked Precursors **10**$^+$ and **11**$^+$ and of the Catenanes **12**$^+$, **13**$^+$, **14**$^+$, and **15**$^+$



aliquots of a solution of dipyridyl ligand (**2** or **3**) in toluene ($c \approx 10^{-5}$ M) were gradually added, and UV−vis spectra were recorded. As expected, upon axial coordination of pyridyl ligands, the absorption bands of zinc(II) porphyrins displayed a bathochromic shift of a few nanometers,[14,16] and the presence of an isosbestic point showed that only one species was formed. The UV−vis absorption spectra obtained during the titration of **1** with increasing amount of **3** are reported in Figure 3.

When no more evolution of the spectrum was detected, the titration was stopped and the data were analyzed with Specfit. The stability constants for the complexes corresponding to the following equilibra were determined:

(16) Flamigni, L.; Ventura, B.; Oliva, A. I.; Ballester, P. *Chem.—Eur. J.* **2008**, *14*, 4214–4224.

$$A + B \rightleftharpoons A \cdot B \quad K_{a1} = \frac{[A \cdot B]}{[A] \times [B]} \qquad (1)$$

A: **1** or $\mathbf{10}^+$ and B: **2** or **3**; thus A · B: **8**,**9**,$\mathbf{10}^+ \cdot \mathbf{2}$ or $\mathbf{10}^+ \cdot \mathbf{3}$

$$A \cdot B + B \rightleftharpoons A \cdot B^2 \quad K_{a2} = \frac{[A \cdot B^2]}{[A \cdot B] \times [B]} \qquad (2)$$

A: $\mathbf{10}^+ \cdot \mathbf{2}$ or $\mathbf{10}^+ \cdot \mathbf{3}$ and B: **2** or **3**; thus A · B: $\mathbf{12}^+$ or $\mathbf{15}^+$

Table 1. Association Constants of **8**, **9**, $\mathbf{12}^+$, and $\mathbf{15}^+$

compd	log K_{a1}	log K_{a2}
8[a]	4.87 ± 0.01	
9[b]	7.03 ± 0.03	
$\mathbf{12}^{+}$[c]	6.0 ± 0.3	6.5 ± 0.2
$\mathbf{15}^{+}$[d]	7.8 ± 0.2	6.6 ± 0.2

[a] Conditions: $[\mathbf{1}]_0 = 1.09 \times 10^{-6}$ M, $[\mathbf{2}] = 5.68 \times 10^{-4}$ M, toluene, room temperature. [b] Conditions: $[\mathbf{1}]_0 = 1.09 \times 10^{-6}$ M, $[\mathbf{3}] = 3.26 \times 10^{-5}$ M, toluene, room temperature. [c] Conditions: $[\mathbf{10}^+]_0 = 7.97 \times 10^{-7}$ M, $[\mathbf{2}] = 4.63 \times 10^{-5}$ M, toluene, room temperature. [d] Conditions: $[\mathbf{10}^+]_0 = 7.62 \times 10^{-6}$ M, $[\mathbf{3}] = 2.29 \times 10^{-5}$ M, toluene, room temperature.

The various values obtained are reported in Table 1.

These results show that the noncovalent macrocycle **9** is significantly more stable than **8**. In fact, in the macrocyclic assembly **9,** there is a perfect distance and angle complementarity between its two components **1** and **3**. In **1**, the average angle between the two porphyrins linked on a 2,9-diphenyl-1,10-phenanthroline is 60°. As pyridines coordinate zinc porphyrins approximately orthogonally, in order to have the best fit the two pyridyl group axes borne by the spacer must form an angle of 120°. This is the case for **3** where the two pyridines are linked on positions 2 and 7 of the naphthalene nucleus, whereas in **2** the 1,10-phenanthroline spacer connects the two pyridyls with an angle of 60°. Thus, in **8** the geometrical match is less good between its two components **1** and **2** and the system is less stable. This trend is also observed for catenanes $\mathbf{12}^+$ and $\mathbf{15}^+$. As catenane $\mathbf{12}^+$ is the kinetic product of the reaction of $\mathbf{10}^+$ with 2 equiv of **2**, and since the rearrangement to $\mathbf{13}^+$ occurs only after one night, we conclude that at the time scale of the UV−vis experiment the association constant of $\mathbf{12}^+$ only is measured.

Conclusion

In conclusion, by using two types of coordination bonds, namely the copper(I)−1,10-phenanthroline interaction and the pyridine−Zn bond, we could synthesize sophisticated catenanes in high yield, either as kinetic products or, after a certain equilibration period, as thermodynamic products. The present study also stresses the importance of geometrical factors in non covalently assembled edifices built using coordination chemistry. Contrary to systems based on hydrogen bonds, which are only weakly dependent on the direction of the interaction,[17] metal−ligand interaction is relatively demanding in terms of distances and angles, even for first-row transition metals. As shown, by the comparison between the stability constants of $\mathbf{12}^+$ (bad geometrical fit between the components) and $\mathbf{15}^+$ (perfect fit), it is necessary to design large coordination chemistry-assembled species in a very precise way from a geometrical viewpoint, as already shown by others[18] and as pioneered by the groups of Fujita[19] and Stang,[20] in particular.

Experimental Section

General Methods. Dry solvents were distilled from suitable drying agents (1,2-dimethoxyethane and toluene from sodium/benzophenone and dichloromethane from calcium hydride). Thin-layer chromatography was carried out using precoated polymeric sheets of silica gel (Macheray-Nagel, POLYGRAM, SIL G/UV_{254}). Preparative column chromatography was carried out using silica gel (Merck Kieselgel, silica gel 60, 0.063−0.200 mm). Automatic flash column chromatography was carried out on an Isco Combiflash Retrieve machine with prepacked RediSep silica columns. Nuclear magnetic resonance (NMR) spectra for ^{1}H were acquired on Bruker AVANCE 500, 400, or 300 spectrometers. The spectra were referenced to residual proton-solvent references (^{1}H: CD_2Cl_2 at 5.32 ppm, $CDCl_3$: 7.26 ppm). In the assignments, the chemical shift (in ppm) is given first, followed, in parentheses, by the multiplicity of the signal (s: singlet, d: doublet, t: triplet, m: multiplet, bd: broad doublet), the number of protons implied, the value of the coupling constants in hertz, if applicable, and finally the assignment. Mass spectra were obtained by using a Bruker MicroTOF spectrometer (ES-MS).

Starting Materials. All chemicals were of best commercially available grade and used without further purification (unless mentioned). 2,9-Dichloro-1,10-phenanthroline is prepared on a gram scale in three steps from 1,10-phenanthroline monohydrate as already described.[13]

Spectral and Equilibrium Constant Measurements. UV−vis spectra were recorded with a Kontron Instruments UVIKON 860 spectrometer at 25 °C with 1 cm path cell. All measurements were made in toluene solutions, $c \approx 10^{-6}$ M in bis-zinc derivative **1** or $\mathbf{10}^+$. Dipyridyl ligands **2** or **3** in toluene solutions ($c \approx 10^{-5}$ M) were added to the bis-zinc derivative sample in 10 μL aliquots via a 100-μL Hamilton syringe. UV−vis spectrophotometric titrations were analyzed by fitting the series of spectra at 1 nm intervals by using the SPECFIT/32 3.0 (Spectrum Software Associates) which takes into account the changes in volume during the titration.

Compound 2. A Schlenck flask was charged with 2,9-dichloro-1,10-phenanthroline (25 mg, 0.1 mmol), pyridine-4-boronic acid (27 mg, 0.22 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol). The mixture was degassed by three vacuum-argon cycles, dissolved in 1 mL of freshly distilled and degassed DME and 0.1 mL of a degassed aqueous solution of 2 N Na_2CO_3 and heated at reflux overnight. The solvents were evaporated under reduced pressure and the crude product taken up in CH_2Cl_2 and washed with water (3x 10 mL). The organic layers were dried under vacuum. The resulting material was purified by flash column chromatograhy on silica eluted with CH_2Cl_2/MeOH (100/0 to 98/2) to yield **2** as a white solid (28 mg, 84%): ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K) δ (ppm) 8.87 (d, 4 H,

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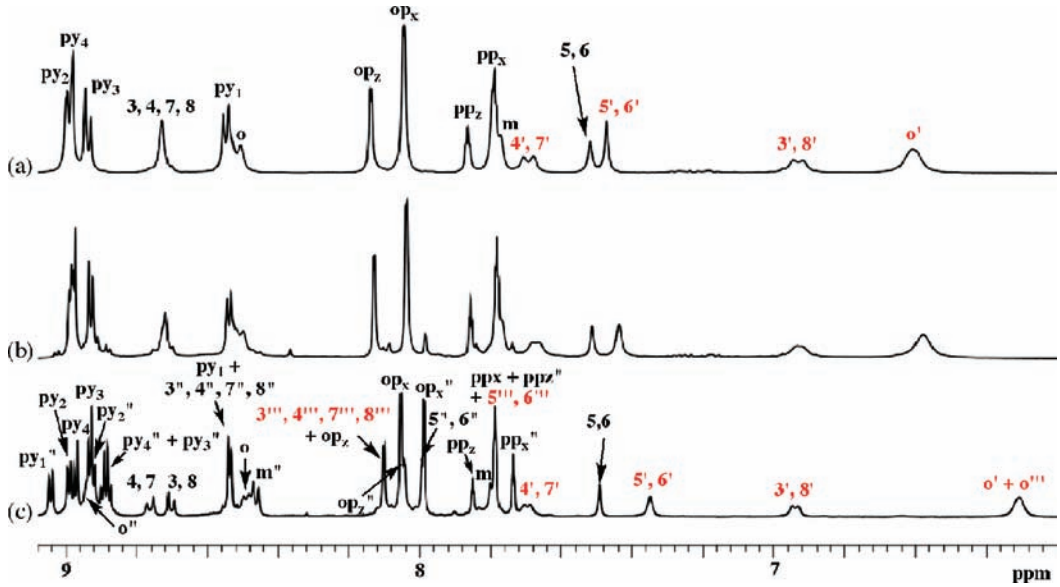

Figure 1. Partial ^{1}H NMR spectrum (500 MHz, CD_2Cl_2, 25 °C) of (a) **12**$^+$, (b) 80% of **12**$^+$ and 20% of **13**$^+$, (c) **13**$^+$. The numbering scheme of the various protons is shown in Scheme 4.

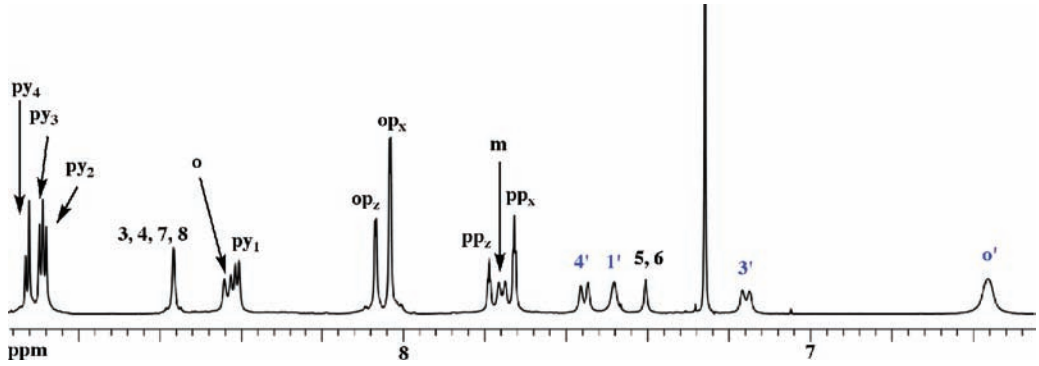

Figure 2. Partial ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 °C) of **15**$^+$. The numbering scheme of the various protons is shown in Scheme 4.

^3J = 6.2 Hz, m), 8.47 (d, 2 H, ^3J = 8.5 Hz, 4, 7), 8.35 (d, 4 H, ^3J = 6.2 Hz, o), 8.26 (d, 2 H, ^3J = 8.5 Hz, 3, 8), 7.94 (s, 2 H, 5, 6); ES/MS *m*/*z* 335.13 (**2** + H^+), calcd 335.39 for $C_{22}H_{14}N_4 + H^+$.

Compound 3. A round-bottom flask charged with methanesulfonic acid 1,1,1-trifluoro-1,1′-(2,7-naphthalenediyl) ester **7** (321 mg, 0.76 mmol) and $Pd(PPh_3)_4$ (53 mg, 6 mol %) was degassed by three vacuum−argon cycles. The mixture was dissolved in 10 mL of freshly distilled and degassed toluene. A degassed solution of pyridine-4-boronic acid (279 mg, 2.27 mmol) in EtOH (10 mL) and a degassed solution of Na_2CO_3 (403 mg, 3.80 mmol) in deionized water (2 mL), respectively, were then added. The mixture was heated at 90 °C overnight under argon. The solvents were evaporated under reduced pressure, and the crude product was taken up in CH_2Cl_2 and washed with water (3 × 30 mL). The organic layers were dried with $MgSO_4$. The resulting material was purified by column chromatograhy on silica eluted with CH_2Cl_2/MeOH (100/0 to 95/5) and precipitated with CH_2Cl_2/heptane to give a white solid **3** (130 mg, 60%): ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm) 8.74 (d, 4 H, ^3J = 6.3 Hz, m), 8.22 (d, 2 H, ^4J = 1.8 Hz, 1), 8.03 (d, 2 H, ^3J = 8.7 Hz, 4), 7.82 (dd, 2 H, ^3J = 8.7 Hz, ^4J = 1.8 Hz, 3), 7.68 (d, 4 H, ^3J = 6.3 Hz, o); ES/MS *m*/*z* 283.122 (**3** + H^+), calcd 283.123 for $C_{20}H_{14}N_2 + H^+$.

Compound 8. A round-bottom flask was charged with **1** (10 mg, 0.0045 mmol) and **2** (1.5 mg, 0.0045 mmol) and degassed by three vacuum−argon cycles. The mixture was dissolved in 1 mL of freshly distilled and degassed CH_2Cl_2. The mixture was allowed to react for 3 h at room temperature under argon. The solvent was removed under reduced pressure and the crude product dried under vacuum to yield quantitatively a purple-greenish solid **8** (11.5 mg): ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) δ (ppm) 9.03 (d, 4 H, ^3J = 4.7 Hz, py_1), 8.94 (d, 4 H, ^3J = 8.7 Hz, o), 8.90 (d, 4 H, ^3J = 4.7 Hz, py_4), 8.91 (d, 4 H, ^3J = 4.6 Hz, py_3), 8.88 (d, 4 H, ^3J = 4.7 Hz, py_2), 8.54 (bs, 4 H, 3, 8 + 4, 7), 8.46 (d, 4 H, ^3J = 8.7 Hz, m), 8.10 (d, 4 H, ^4J = 1.6 Hz, op_z), 8.00 (s, 2 H, 5, 6), 7.98 (d, 8 H, ^4J = 1.6 Hz, op_x), 7.81 (t, 2 H, ^4J = 1.7 Hz, pp_z), 7.73 (t, 4 H, ^3J = 1.7 Hz, pp_x), 7.46 (bd, 2 H, ^3J = 8.2 Hz, 4′, 7′), 7.04 (s, 2 H, 5′, 6′), 7.03 (bd, 2 H, ^3J = 7.6 Hz, 3′, 8′), 6.69 (bs, 4 H, o′), 4.85 (vbs, 4 H, m′), 1.51 (s, 36 H, *t*-Bu_z), 1.40 (s, 72 H, *t*-Bu_x); ES/MS *m*/*z* 2539.83 (**8** + H^+), calcd 2539.24 for $C_{170}H_{170}N_{14}Zn_2 + H^+$.

Compound 9. In a round-bottom flask, **1** (6.6 mg, 0.003 mmol) was dissolved in 2 mL of freshly distilled and degassed CH_2Cl_2. In a round-bottom flask, **3** (5 mg) was dissolved in 3 mL of freshly distilled and degassed CH_2Cl_2. A 0.5 mL (0.003 mmol) portion of this solution was added dropwise to the solution of **1** in CH_2Cl_2. The solution turned immediately purple-green. The mixture was allowed to react for 3 h at room temperature under argon. The solvent was removed under reduced pressure to afford quantitatively the desired complex as a purple greenish solid **9** (7.4 mg): ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ (ppm) 8.98 (d, 4 H, ^3J = 4.7 Hz, py_1), 8.93 (d, 4 H, ^3J = 4.7 Hz, py_4), 8.91 (d, 4 H, ^3J = 4.5 Hz, py_3), 8.89 (d, 4 H, ^3J = 4.5 Hz, py_2), 8.83 (d, 4 H, ^3J = 8.7 Hz, o), 8.48 (d, 4 H, ^3J = 8.6 Hz, m), 8.47 (bs, 4 H, 3, 8 + 4, 7), 8.09 (d, 4 H, ^4J = 1.7 Hz, op_z), 8.00 (d, 8 H, ^4J = 1.8 Hz, op_x), 7.95 (s, 2 H, 5, 6), 7.76 (t, 2 H, ^4J = 1.8 Hz, pp_z), 7.71 (t, 4 H, ^3J = 1.8 Hz, pp_x), 7.34 (bd, 2 H, ^3J = 8.3 Hz, 4′), 7.04 (bd, 2 H, ^4J = 1.8 Hz,

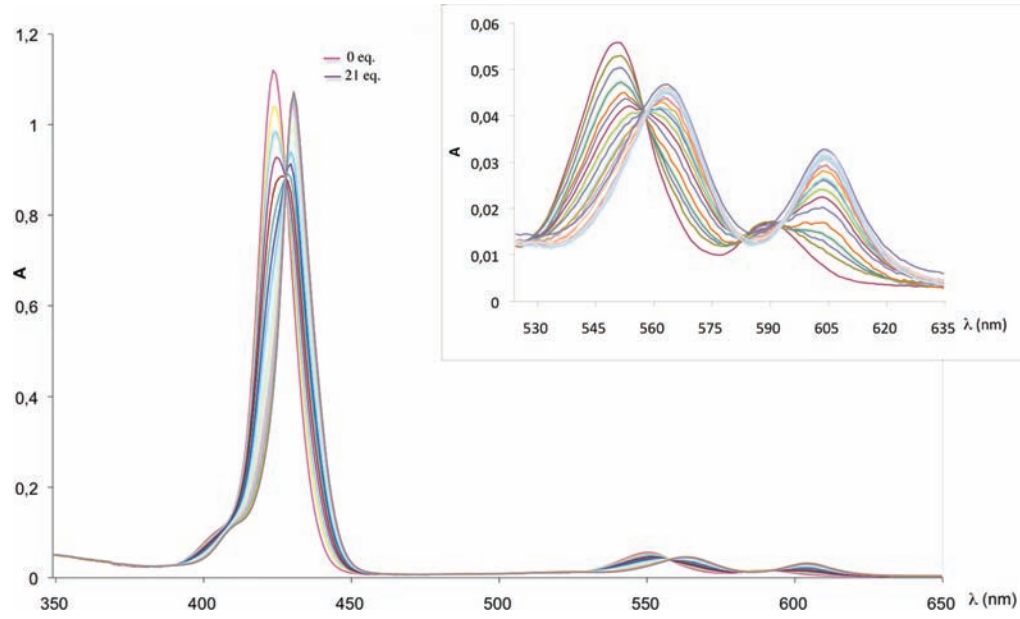

Figure 3. Absorption spectra in toluene containing **1** (1.09×10^{-6} M, 3 mL) after additions of constant aliquots (10 μL) of **3** (stock solution: 3.26×10^{-5} M). The inset is an expansion of the Q band region.

1′), 6.81 (bd, 2 H, $^3J = 8.7$ Hz, $^4J = 1.8$ Hz, 3′), 5.97 (bs, 4 H, o′), 3.22 (vbs, 4 H, m′), 1.52 (s, 36 H, *t*-Bu$_z$), 1.45 (s, 72 H, *t*-Bu$_x$).

Compound 10·PF$_6$. In a round-bottom flask, **1** (50.2 mg, 0.023 mmol) was dissolved in 5 mL of freshly distilled CH_2Cl_2. The solution was degassed by three vacuum−argon cycles. In a Schlenck flask, $Cu(CH_3CN)_4 \cdot PF_6$ (5.1 mg, 0.014 mmol) was dissolved in 7 mL of degassed CH_3CN. This solution was added via cannula to the solution of **1** in CH_2Cl_2. The mixture was allowed to react for 3 h at room temperature under argon. The solvents were removed under reduced pressure, and the purple solid was taken up with CH_2Cl_2 and washed with water (2 × 5 mL). The organic layers were dried under vacuum, and 53 mg of a purple solid **10·PF$_6$** was obtained (100%): ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K) δ (ppm) 9.05 (d, 8 H, $^3J = 4.7$ Hz, py$_2$), 9.03 (d, 8 H, $^3J = 4.8$ Hz, py$_4$), 9.02 (d, 8 H, $^3J = 4.7$ Hz, py$_3$), 8.68 (bs, 8 H, 3, 8 + 4, 7), 8.54 (d, 8 H, $^3J = 8.7$ Hz, o), 8.52 (d, 8 H, $^3J = 4.8$ Hz, py$_1$), 8.13 (m, 24 H, op$_z$ + op$_x$), 7.90 (t, 4 H, $^4J = 1.7$ Hz, pp$_z$), 7.86 (t, 8 H, $^4J = 1.7$ Hz, pp$_x$), 7.82 (d, 8 H, $^3J = 8.1$ Hz, m), 7.43 (s, 4 H, 5, 6), 1.57 (s, 72 H, *t*-Bu$_z$), 1.54 (s, 144 H, *t*-Bu$_x$); ES/MS *m*/*z* 4475.56 (**10**$^+$), calcd 4474.97 for $C_{296}H_{312}N_{20}CuZn_4$.

Compound 11·PF$_6$. In a round-bottom flask, **2** (14.6 mg, 0.044 mmol) was dissolved in 5 mL of freshly distilled CH_2Cl_2. The solution was degassed by three vacuum−argon cycles. In a Schlenck flask, $Cu(CH_3CN)_4 \cdot PF_6$ (19.5 mg) was dissolved in 15 mL of degassed CH_3CN. A 7.5 mL (0.026 mmol) portion of this solution was added dropwise to the solution of **2** in CH_2Cl_2. The solution turned immediately red. The mixture was allowed to react for 3 h at room temperature under argon. The solvents were removed under reduced pressure, and the crude product was taken up in CH_2Cl_2 and washed with water (2 × 5 mL). The organic layers were dried under vacuum to yield the desired complex **11·PF$_6$** as a deep red solid (15.7 mg, 81%): ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K) δ (ppm) 8.72 (d, 4 H, $^3J = 8.4$ Hz, 4, 7), 8.20 (s, 4 H, 5,6), 8.04 (d, 4 H, $^3J = 8.4$ Hz, 3, 8), 7.92 (b, 8 H, m), 7.32 (b, 8 H, o); ES/MS *m*/*z* 731.18 (**11**$^+$) calcd 732.24 for $C_{44}H_{28}N_8Cu$.

Compound 12·PF$_6$. A round-bottom flask was charged with **10·PF$_6$** (13.8 mg, 0.003 mmol) and **2** (2 mg, 0.006 mmol) and degassed by three vacuum−argon cycles. The mixture was dissolved in 2 mL of freshly distilled and degassed CH_2Cl_2. The mixture was allowed to react for 3 h at room temperature under argon. The solvent was removed under reduced pressure and the crude product dried under vacuum to yield quantitatively a purple-greenish solid **12·PF$_6$** (15.8 mg): ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K) δ (ppm) 9.03 (d, 8 H, $^3J = 4.7$ Hz, py$_2$), 9.01 (d, 8 H, $^3J = 4.8$ Hz, py$_4$), 8.98 (d, 8 H, $^3J = 4.7$ Hz, py$_3$), 8.76 (bs, 8 H, 3, 8 + 4, 7), 8.58 (d, 8 H, $^3J = 4.7$ Hz, py$_1$), 8.56 (d, 8 H, $^3J = 8.7$ Hz, o), 8.17 (d, 8 H, $^4J = 1.6$ Hz, op$_z$), 8.08 (d, 16 H, $^4J = 1.6$ Hz, op$_x$), 7.90 (t, 4 H, $^4J = 1.7$ Hz, pp$_z$), 7.83 (m, 16 H, $^3J = 1.7$ Hz, pp$_x$ + m), 7.73 (bd, 4 H, $^3J = 8.2$ Hz, 4′, 7′), 7.55 (s, 4 H, 5, 6), 7.50 (s, 4 H, 5′, 6′), 6.96 (bd, 4 H, $^3J = 7.6$ Hz, 3′, 8′), 6.65 (bs, 8 H, o′), 4.40 (vbs, 8 H, m′), 1.60 (s, 72 H, *t*-Bu$_z$), 1.50 (s, 144 H, *t*-Bu$_x$); ES/MS *m*/*z* 2572.20 (**12**$^+$ + H$^+$)/2, calcd 5144.74 for $C_{340}H_{340}N_{28}CuZn_4$ + H$^+$; UV−vis (toluene) λ_{max} (log ε) = 430 (6.07), 561 (4.79), 606 (4.60) nm.

The pure compound was dissolved into CD_2Cl_2 overnight, and the next day, signals of **13·PF$_6$** were detected by NMR. Finally a ratio of 80% of **12**$^+$ and 20% of **13**$^+$ was reached after 1 day.

Compound 13·PF$_6$. In a round-bottom flask, **11·PF$_6$** (2.1 mg) was dissolved in 1 mL of freshly distilled and degassed CH_2Cl_2. A 0.76 mL (0.018 mmol) portion of this solution was added dropwise to a solution of **1** (8 mg, 0.036 mmol) in 0.5 mL of freshly distilled and degassed CH_2Cl_2. The mixture was allowed to react overnight at room temperature under argon. The solvent was removed under reduced pressure and the crude product dried under vacuum to give quantitatively a purple-greenish solid **13·PF$_6$**: ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) δ (ppm) 9.05 (d, 4 H, $^3J = 4.6$ Hz, py$_1$″), 9.00 (d, 4 H, $^3J = 4.6$ Hz, py$_2$), 8.98 (d, 4 H, $^3J = 4.6$ Hz, py$_4$), 8.94 (d, 4 H, $^3J = 8.7$ Hz, o″), 8.94 (d, 4 H, $^3J = 4.6$ Hz, py$_3$), 8.93 (d, 4 H, $^3J = 4.8$ Hz, py$_2$″), 8.90 (d, 4 H, $^3J = 4.6$ Hz, py$_4$″), 8.88 (d, 4 H, $^3J = 4.8$ Hz, py$_3$″), 8.77 (d, 2 H, $^3J = 8.1$ Hz, 4,7), 8.71 (d, 2 H, $^3J = 8.3$ Hz, 3,8), 8.54 (bs, 4 H, 3″,8″ + 4″,7″), 8.54 (d, 4 H, $^3J = 4.4$ Hz, py$_1$), 8.49 (bd, 4 H, $^3J = 7.7$ Hz, o), 8.47 (d, 4 H, $^3J = 8.3$ Hz, m″), 8.11 (bs, 4 H, 3‴,8‴ + 4‴,7‴), 8.10 (d, 4 H, $^4J = 1.7$ Hz, op$_z$), 8.06 (d, 8 H, $^4J = 1.7$ Hz, op$_x$), 8.05 (d, 4 H, $^4J = 1.5$ Hz, op$_z$″), 8.00 (s, 2 H, 5″,6″), 7.99 (d, 8 H, $^4J = 1.8$ Hz, op$_x$″), 7.85 (t, 2 H, $^4J = 1.7$ Hz, pp$_z$), 7.79 (d, 4 H, $^3J = 7.7$ Hz, m), 7.79 (m, 8 H, pp$_x$ + pp$_z$″ + 5‴,6‴), 7.74 (d, 2 H, $^4J = 1.8$ Hz, pp$_x$″), 7.70 (bd, 2 H, $^3J = 8.3$ Hz, 4′,7′), 7.49 (s, 2 H, 5,6), 7.35 (s, 2 H, 5′,6′), 6.94 (bd, 2 H, $^3J = 8.3$ Hz, 3′,8′), 6.31 (bs, 8 H, o′ + o‴), 3.52 (vbs, 8 H, m′ + m‴), 1.54 (s, 36 H, *t*-Bu$_z$), 1.50 (s, 36 H, *t*-Bu$_z$″), 1.49 (s, 72 H, *t*-Bu$_x$), 1.41 (s, 72 H, *t*-Bu$_x$″); UV−vis (toluene) λ_{max} (log ε) = 428 (6.07), 556 (4.79), 603 (4.60) nm.

The compound was dissolved in 0.4 mL of CD_2Cl_2, and the solution was monitored by ^{1}H NMR. After 2 weeks, no more change was observed, and the ratio 65% of **12**$^+$ and 35% of **13**$^+$ was reached.

Compound 15·PF$_6$. In a round-bottom flask, **10·PF$_6$** (6.6 mg, 0.003 mmol) was dissolved in 1 mL of freshly distilled and degassed CH_2Cl_2. In a round-bottom flask, **3** (4 mg) was dissolved in 4 mL of freshly distilled and degassed CH_2Cl_2. A 1.2 mL (0.0042 mmol) portion of this solution was added dropwise to the solution of **10·PF$_6$** in CH_2Cl_2. The solution turned immediately purple-green. The mixture was allowed to react for 1 h at room temperature under argon. The solvent was removed under reduced pressure to give quantitatively the desired complex **15·PF$_6$** as a purple greenish solid (11 mg): ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ (ppm) 8.93 (d, 8 H, ^3J = 4.4 Hz, py_4), 8.89 (d, 8 H, ^3J = 4.3 Hz, py_3), 8.88 (d, 8 H, ^3J = 4.0 Hz, py_2), 8.57 (bs, 8 H, 3, 8 + 4, 7), 8.43 (d, 8 H, ^3J = 8.1 Hz, m), 8.41 (d, 8 H, ^3J = 4.4 Hz, py_1), 8.07 (d, 8 H, ^4J = 1.7 Hz, op_z), 8.05 (d, 16 H, ^4J = 1.7 Hz, op_x), 7.79 (t, 4 H, ^4J = 1.7 Hz, pp_z), 7.76 (d, 8 H, ^3J = 7.9 Hz, m), 7.73 (m, 8 H, ^3J = 1.7 Hz, pp_x), 7.56 (bd, 4 H, ^3J = 8.7 Hz, 4′), 7.48 (bs, 4 H, 1′), 7.41 (s, 4 H, 5, 6), 7.16 (bd, 4 H, ^3J = 8.4 Hz, 3′), 6.56 (bs, 8 H, o′), 5.22 (vbs, 8 H, m′), 1.53 (s, 72 H, *t*-Bu_z), 1.46 (s, 144 H, *t*-Bu_x).

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Supporting Information Available: ^{1}H NMR spectra including COSY and ROESY data of compounds **8**, **9**, **12·PF$_6$**, **13·PF$_6$**, and **15·PF$_6$**; UV−vis spectra for **12·PF$_6$** and **13·PF$_6$**. This material is available free of charge via the Internet at http://pubs.acs.org.

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