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Dynamics of Closure of Zinc Bis-Porphyrin Molecular Tweezers with Copper(II) Ions and Electron Transfer

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Abstract: Zinc bis-porphyrin molecular tweezers composed of a N_4 spacer bound through pyridyl units to the *meso* position of porphyrins were synthesized, and the tweezers are closed by the coordination of a copper(II) ion inside the spacer ligand. The effect of the π–π interaction between the porphyrin rings in the closed conformation on the absorption spectra of multi-electron oxidized species and the reduction potentials were clarified by chemical and electrochemical oxidation of the closed form of the zinc bis-porphyrin molecular tweezers in comparison with the open form without copper(II) ion and the corresponding porphyrin monomer. The shifts in redox potentials and absorption spectrum of the porphyrin dication indicate a strong electronic interaction between the two oxidized porphyrins in the closed form, whereas there is little interaction between them in the neutral form. The dynamics of copper(II) ion coordination and subsequent electron transfer was examined by using a stopped-flow UV/Vis spectroscopic technique. It was confirmed that coordination of copper(II) occurs prior to electron-transfer oxidation of the closed form of the zinc bis-porphyrin molecular tweezers.

Keywords: copper · electron transfer · pi interactions · porphyrinoids · zinc

Introduction

The crucial role of cofacial porphyrinoid dimers in the structure of the photosynthetic reaction center has stimulated extensive studies on mimics of this reaction center.[1–9] Strong π–π interactions exist between the two macrocycles of the special pair, in particular when it is oxidized to the radical cation.[1,3] The electron-transfer properties of cofacial porphyrin dimers are known to be significantly enhanced due to π-electron delocalization in the dimer radical cations.[10,11] Delocalization of π electrons between discrete π systems is well known not only in porphyrin dimer radical cations but also in aromatic dimer radical cations in general.[12–16] Such delocalization of π electrons has recently been reported to be finely controlled by anion binding in a supramolecular π system based on a tetrathiafulvalene calix[4]pyrrole (an electron donor) and a dicationic bis-imidazolium quinone (an electron acceptor), wherein anion binding to the donor promotes electron transfer by inducing a conformational change that facilitates the π–π interaction in the π-dimer radical cation.[17] In contrast to the anion binding, the cation binding inhibits the π–π interaction to reverse the direction of electron transfer.[17]

On the other hand, copper(I) ions have frequently been utilized in the template synthesis of porphyrin catenanes and rotaxanes in which the energy-transfer and electron-transfer processes in the interlocked structures can be controlled by the absence or presence of a copper(I) ion.[18,19] Geometry control of the π–π interaction between π compounds has also been made possible by metal-ion coordination.[20–22] Such a change in the π–π interaction is expected to affect the redox properties of the π compounds. However, the change in the redox properties associated with the geometry control of the π–π interaction between π compounds by metal-ion coordination has yet to be studied. In addition, there has been no report on the dynamics of metal-ion binding that induces the conformational change, although the dynamics of anion binding to diprotonated cyclo[8]pyrrole has recently been reported.[23]

We report herein geometry control of π–π interaction between two π components by a metal ion which coordinates

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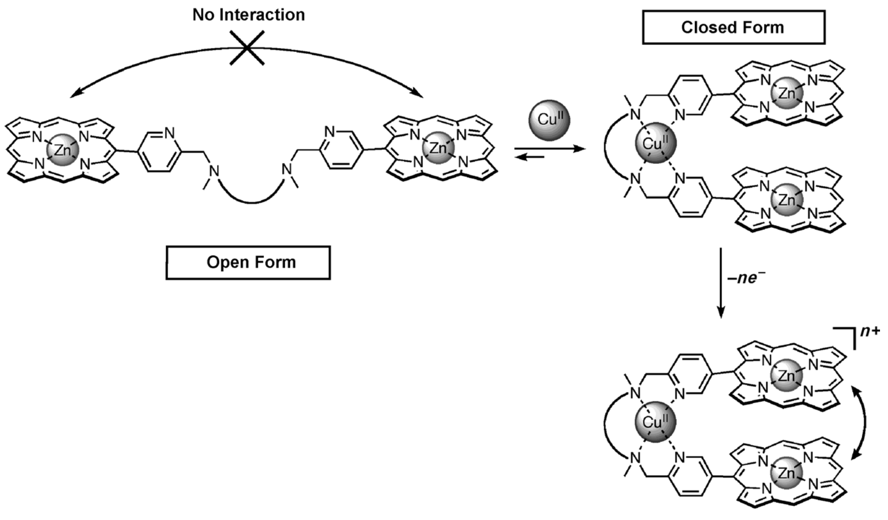
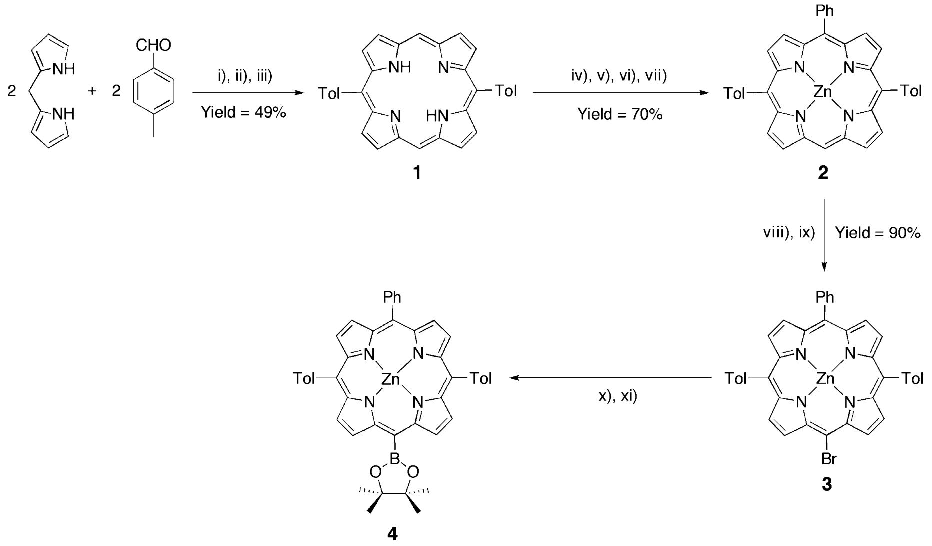
to the linker ligand of the two π components, and the dynamics of metal coordination followed by electron transfer. We chose zinc bis-porphyrin molecular tweezers composed of an N_4 spacer bound through pyridyl units to the *meso* position of porphyrins.[24] Closure of the tweezers from the open form is made possible by the coordination of copper(II) ion to the linker ligand, as shown in Scheme 1. In the closed form, the enhanced π–π interaction between two porphyrins of the zinc bis-porphyrin is clearly recognized in the oxidized states, as indicated by the shift in the absorption spectrum compared with the open form without copper(II) ion. The changes in the oxidation potentials of the bis-porphyrin on the coordination of a copper(II) ion to the linker ligand were examined by cyclic voltammetry in comparison with the porphyrin monomer. The dynamics of the closure of the tweezers by coordination of the copper(II) ion to the linker ligand and subsequent electron transfer from copper(II) ion to the zinc porphyrin units in the closed form have been examined for the first time. This study provides an excellent way not only to control the geometry between the porphyrin rings by coordination of copper(II) ion, but also dynamics of the coordination of copper(II) ion and the resulting electron transfer.



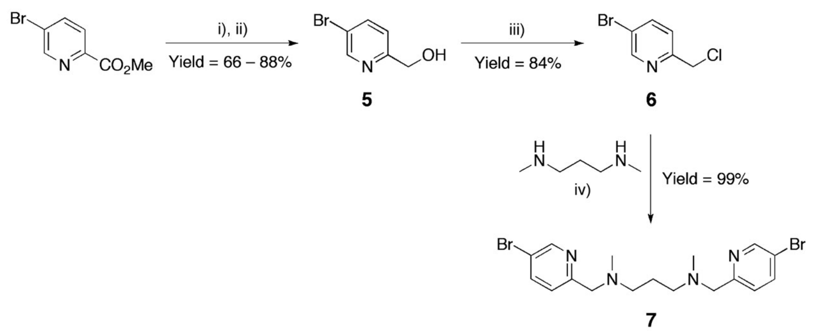
Scheme 1. Closure of a zinc bis-porphyrin tweezer from the open form by the coordination of copper(II) ion, and structural change induced by electron-transfer oxidation.

Results and Discussion

Synthesis of zinc bis-porphyrin molecular tweezers: Syntheses of *trans*-AB_2C boronated porphyrin **4** and dibrominated spacer **7** are shown in Schemes 2 and 3, respectively. Several methods have been reported for the synthesis of *trans*-AB_2C porphyrins. Statistical methods[25] are the most direct pathway to obtain these derivatives, but purification by column chromatography is often difficult and the yields are relatively low. Combination of the methods of Woodward and MacDonald and Markovac[26] with that of Senge et al.[27] is a more elegant alternative, despite the fact that more synthetic steps are required to access the final derivative, which is formed by condensation of 2 equivalents of dipyrromethane with 2 equivalents of aldehyde in dichloromethane catalyzed by trifluoroacetic acid. It is well-known in the literature that such a reaction usually leads to some scrambling. As a consequence, the purification steps are often difficult and therefore yields are low. For the synthesis of 5,15-di-*p*-tolylporphyrin (**1**), two strategies are possible: 1) reaction of 5-*p*-tolyldipyrromethane with formaldehyde and 2) condensation of 5-dihydrodipyrromethane with *p*-tolualdehyde. We explored only the second strategy, for two reasons. Firstly 5-dihydrodipyr-



Scheme 2. Synthesis of boronated porphyrin **4**. Conditions: i) TFA, CH_2Cl_2; ii) *p*-chloranil; iii) NEt_3; iv) $Zn(OAc)_2{\cdot}2H_2O$, NaOAc, $CHCl_3$, MeOH; v) PhLi (2 M), THF, 0°C; vi) H_2O/THF; vii) DDQ; viii) NBS, py, CH_2Cl_2 0°C; ix) acetone; x) pinacolborane, $[Pd(PPh_3)_2Cl_2]$ (3 mol%), NEt_3, anhydrous DCE; xi) KCl/H_2O (30%).



Scheme 3. Synthesis of spacer **7**. Conditions: i) $NaBH_4$, MeOH; ii) H_2O; iii) $SOCl_2$, toluene; iv) K_2CO_3, MeCN.

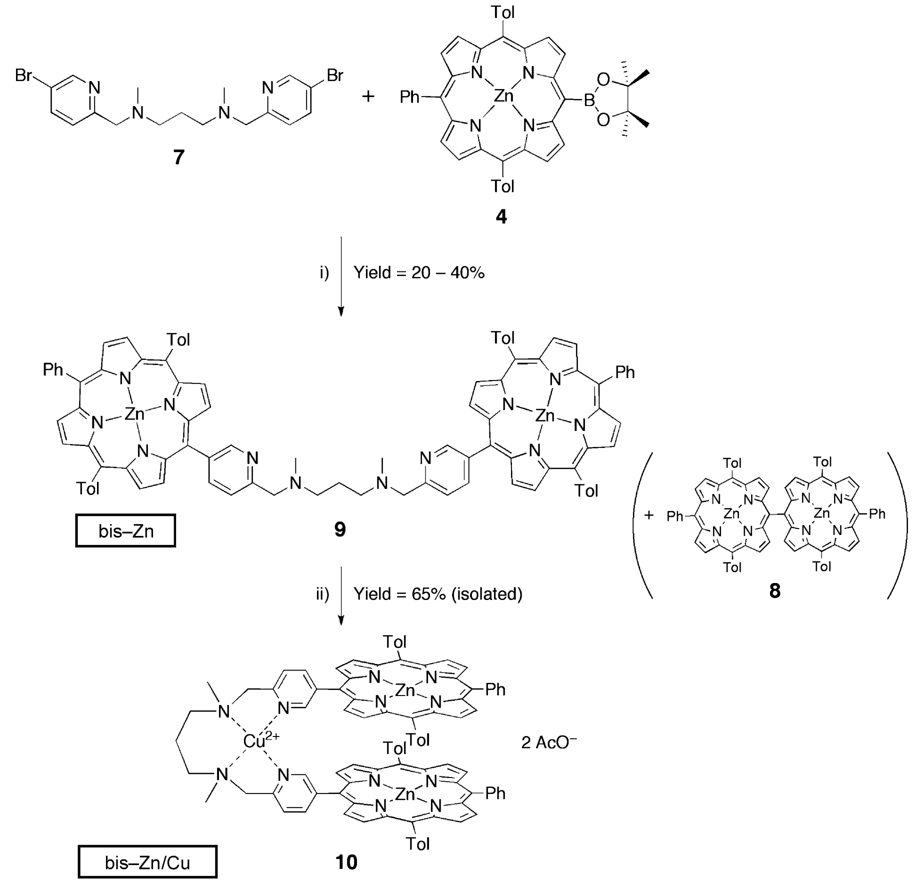
romethane is much more resistant to acidolysis than 5-*p*-tolyldipyrromethane. Therefore, less scrambling is expected. Secondly, synthesis of 5-dihydrodipyrromethane is a high-yield reaction.[28] This strategy allowed us to obtain the desired porphyrin **1** in 49 % yield on the gram scale without any scrambling (Scheme 2).

Afterwards, a third aryl group was selectively introduced at one of the two *meso* positions of **1** by addition of phenyllithium at 0 °C,[27] affording **2** in 70 % yield. The last unsubstituted *meso* position of **2** was then brominated by classical reaction with recrystallized *N*-bromosuccinimide at room temperature in 72 % yield.[29] This reaction was further improved (90 % yield) by decreasing the reaction temperature to 0 °C in the presence of a base. Bromoporphyrin **3** was then quantitatively transformed into **4** by addition of pinacolborane, catalyzed by palladium(II) in anhydrous 1,2-dichloroethane (DCE) in the presence of triethylamine as base (Scheme 2).[30,31]

Dibromo spacer **7** was obtained in high yield according to the reaction pathway in Scheme 3. Key derivative **6** was synthesized by stepwise reduction and chlorination of commercially available methyl 5-bromopyridine-2-carboxylate.

The Suzuki–Miyaura coupling reaction between **4** and **7** is shown in Scheme 4.[30] To perform the coupling reaction between boronated porphyrin **4** and dibrominated spacer **7**, [{PdCl(η^3-C_3H_5)}$_2$] was chosen as precatalyst with PPh_3 as ligand in a toluene/DMF (5/3). Cesium(I) carbonate was used as a base, while sodium iodide was added to the reaction mixture to facilitate the oxidative addition step. Boronated porphyrin **4** was added slowly over 10 h to avoid side reactions such as formation of *meso–meso* porphyrin dimer **8**. Because we observed some instability of spacer **7** in solution, the reaction was carried out with only 1 equivalent of boronated porphyrin **4** and 1 equivalent of spacer **7**, contrary to the stoichiometry of the reaction. Despite this instability of spacer **7**, tweezers bis-Zn **9** could be obtained in 20–40 % yield. It was characterized by ^{1}H NMR, ^{13}C NMR, and UV/Vis spectroscopy, and ESI/TOF HRMS (Figures S1–S3, Supporting Information). The ^{1}H NMR spectra of compounds **1** to **7** are given in the Supporting Information (Figures S4–S10).

Copper(II) was coordinated inside the spacer of bis-Zn **9** by addition of copper(II) acetate monohydrate or copper(II) triflate. The reaction of bis-Zn **9** with copper(II) acetate monohydrate in $CHCl_3$/MeOH (1/1), followed by the purification on silica gel and recrystallization, led to bis-Zn/Cu



Scheme 4. Synthesis of molecular tweezers **9** and **10**. Conditions: {[PdCl(η^3-C_3H_5)]$_2$} (10 mol %), PPh_3 (4 equiv), Cs_2CO_3, NaI, toluene/DMF (5:3); ii) $Cu(OAc)_2{\cdot}H_2O$, $CHCl_3$/MeOH.

10, which was isolated in 65 % yield (Scheme 4). Formation of bis-Zn/Cu **10** was proved by the HRMS (ESI/TOF) spectrum, which exhibited an ionic pattern at 1599.4124 Da corresponding to $[M-2\,OAc]^+$ (4 ppm deviation with respect to calculated mass; Figure S11, Supporting Information).

An EPR spectrum of bis-Zn/Cu **10** in frozen medium (77 K) is shown in Figure S12 of the Supporting Information. This spectrum exhibits typical EPR signals due to the copper(II) ion. The EPR parameters ($g_\perp < g_\parallel = 2.173$, $A_\parallel = 218$ G) indicate that the copper(II) ion of bis-Zn/Cu **10** is coordinated to the spacer with a slightly distorted square-planar geometry.[32]

The UV/Vis spectra of zinc(II) tetra-*p*-tolylporphyrin (TpTP)Zn, bis-Zn **9**, and bis-Zn/Cu **10** are compared in Figure 1. The same absorption maxima are observed for reference monomer (TpTP)Zn and bis-Zn **9**.[33] This indicates that the two porphyrin units of bis-Zn **9** behave separately without any interaction. In contrast, the absorption bands of bis-Zn/Cu **10** are slightly redshifted. Although the interaction between the two porphyrins of bis-Zn/Cu **10** may be weak in the neutral form due to the steric hindrance of the tolyl groups at the *meso* positions,[10] the redshifted absorption bands of bis-Zn/Cu **10** indicate a conformational change.[34]

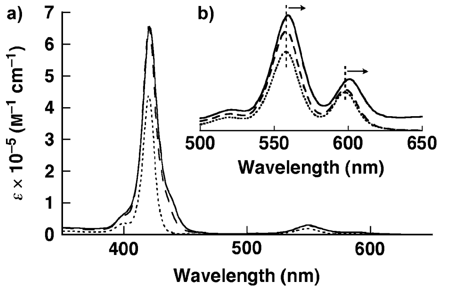


Figure 1. Comparison of a) whole absorption spectra and b) Q bands of (TpTP)Zn (•••••), bis-Zn **9** (-----), and bis-Zn/Cu **10** (——) in CH_2Cl_2 at 298 K.

The optimized structures of bis-Zn **9** and bis-Zn/Cu **10** calculated by DFT are shown in Figure 2. In bis-Zn **9**, the spacer is linear and the porphyrins are far from each other.[35] After insertion of copper(II), the molecular tweezers undergo a structural rearrangement which brings the two porphyrins close to each other. The orientation between the two chromophores is not strictly cofacial but slightly slipped, in agreement with the weak bathochromic shift observed by UV/Vis spectroscopy[34] and X-ray crystal structures of related compounds.[36]

Electrochemical studies: To confirm the structural reorganization and the interactions between the porphyrin units on metalation, the electrochemical behavior of (TpTP)Zn, bis-Zn **9**, and bis-Zn/Cu **10** were investigated. The cyclic voltammogram (CV) of (TpTP)Zn (Figure 3) exhibits two reversible redox waves at 0.35 and 0.75 V (vs. Ag/AgNO$_3$). These one-electron processes are attributed to (TpTP)Zn/$[(TpTP)Zn]^{\cdot+}$ and $[(TpTP)Zn]^{\cdot+}/[(TpTP)Zn]^{2+}$ redox couples, respectively. Two reversible redox waves were also observed for bis-Zn **9**, and the oxidation potentials (0.42 and 0.78 V) are higher than those of (TpTP)Zn due to the influence of the pyridyl group, which is a more electron withdrawing group than a tolyl substituent. Judging from the cur-

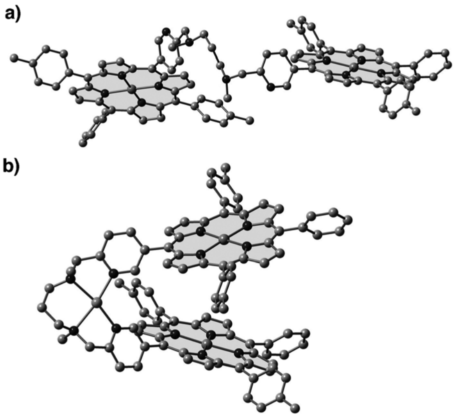


Figure 2. Optimized structures of a) bis-Zn **9** and b) bis-Zn/Cu **10** calculated by DFT (B3LYP/LanL2DZ level). Protons are not shown for clarity.

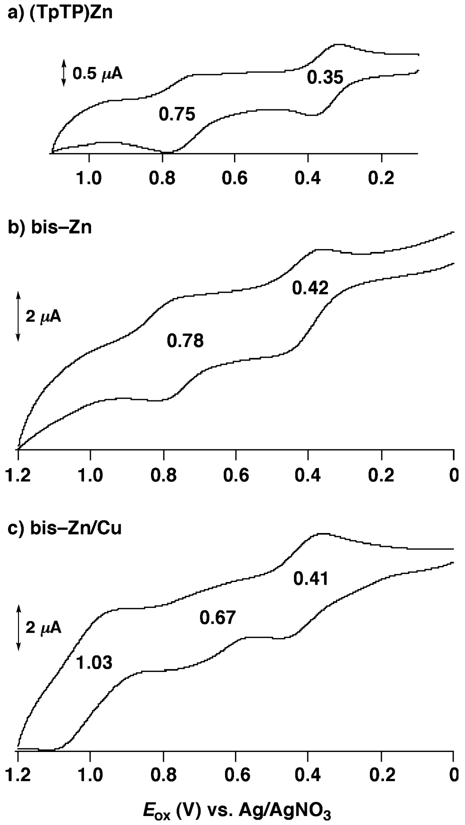


Figure 3. CV of the oxidation part of a) (TpTP)Zn (0.5 mM), b) bis-Zn **9** (1.0 mM), and c) bis-Zn/Cu **10** (1.0 mM) in PhCN containing 0.1 M nBu$_4$NPF$_6$.

rent intensity of each redox process of bis-Zn **9** as compared with that of (TpTP)Zn, each reversible redox wave corresponds to a two-electron process for bis-Zn **9**, that is, there is no interaction between two zinc porphyrin moieties in the open form (bis-Zn **9**).

In contrast to the open form (bis-Zn **9**), the CV and differential pulse voltammogram (DPV) of the closed form (bis-Zn/Cu **10**) shows three oxidation waves (Figure 3c and Figure S13, Supporting Information).[37] The initial oxidation of bis-Zn/Cu **10** at 0.41 V is a two-electron process, similar to that of bis-Zn **9**, while the third and fourth oxidation processes of bis-Zn/Cu **10** are split into two redox waves.[38] Such splittings clearly indicate that the two porphyrin rings interact in the oxidized states.[5b,10,20a,d,39] The fourth oxidation potential of bis-Zn/Cu **10** is considerably shifted in the positive direction because of the electrostatic repulsion between doubly charged porphyrin rings in the closed form of $[\text{bis-Zn/Cu}]^{4+}$.

Reduction of bis-Zn **9** and bis-Zn/Cu **10** was also examined under the same conditions (Figure 4). Bis-Zn **9** undergoes two irreversible reductions at −1.17 and −1.49 V. The first peak can be assigned to reduction of the spacer unit, because reference compound *N*,*N*-bis(pyridin-2-ylmethyl)-propane-1,3-diamine exhibits a similar irreversible cathodic wave at −1.10 V (Figure S15, Supporting Information). The second peak is attributed to reduction of each porphyrin macrocycle leading to the bis-radical dianion $[\text{bis-Zn}]^{2-}$. Similarly, two reduction processes for bis-Zn/Cu **10** at −1.10 and −1.60 V are assigned to reduction of the spacer unit and porphyrin rings, respectively. Another irreversible peak at −0.74 V corresponds to the $\mathrm{Cu^{II}/Cu^{I}}$ process. All electrochemical data of (TpTP)Zn, bis-Zn **9** and bis-Zn/Cu **10** are summarized in Table 1. The electrochemical measurements for a series of porphyrins in PhCN/MeCN (1/1) containing 0.1 м NaOTf are also shown in Figure S16 of the Supporting Information.

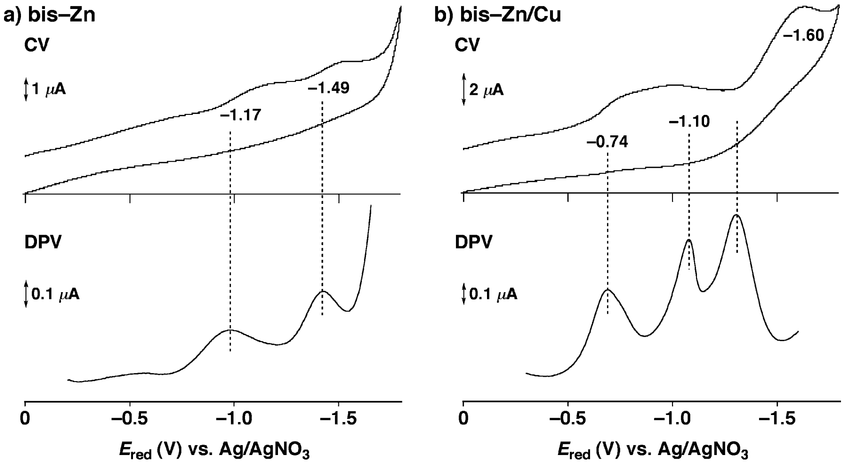


Figure 4. CV and DPV of the reduction part of a) bis-Zn **9** (1.0 mм) and b) bis-Zn/Cu **10** (1.0 mм) in PhCN containing 0.1 м $n\mathrm{Bu_4NPF_6}$.

Table 1. Half-wave and peak potentials* (V vs. $\mathrm{Ag/AgNO_3}$) of the redox center in (TpTP)Zn, bis-Zn 9, and bis-Zn/Cu 10 in PhCN containing 0.1 м $n\mathrm{Bu_4NPF_6}$ at 298 K.

	E_{ox}			E_{red}	
	$\mathrm{Por^{\cdot+}/Por^{2+}}$	$\mathrm{Por/Por^{\cdot+}}$	$\mathrm{Cu^{II}/Cu^{I}}$	Spacer	$\mathrm{Por/Por^{\cdot-}}$
(TpTP)Zn	0.75	0.35	–	–	–
bis-Zn **9**	0.78	0.42	–	−1.17	−1.49*
bis-Zn/Cu **10**	0.67, 1.03	0.41	−0.74*	−1.10	−1.60*

The existence of interactions in the oxidized states is shown by spectrophotometric titration of bis-Zn/Cu **10** by a one-electron oxidant such as $[\mathrm{Ru(bpy)_3}](\mathrm{PF_6})_3$ (bpy = 2,2′-bipyridine).[40] The reduction potential $E_{\mathrm{red}}([\mathrm{Ru(bpy)_3}]^{3+}/[\mathrm{Ru(bpy)_3}]^{2+})$ is 1.25 V (vs. SCE) in PhCN containing 0.1 м $n\mathrm{Bu_4NPF_6}$. Figure S18 (Supporting Information) shows the spectral changes of (TpTP)Zn on addition of $[\mathrm{Ru(bpy)_3}]^{3+}$ in PhCN. When 1 equivalent of $[\mathrm{Ru(bpy)_3}]^{3+}$ was added, the spectrum displayed two broad absorption bands located at $\lambda_{\max} = 612$ and 847 nm, which are typically assigned to the radical cation $[(\mathrm{TpTP})\mathrm{Zn}]^{\cdot+}$.[41] On addition of a further equivalent of $[\mathrm{Ru(bpy)_3}]^{3+}$, dication $[(\mathrm{TpTP})\mathrm{Zn}]^{2+}$ is formed and the absorption band at $\lambda_{\max} = 612$ nm disappears, while the absorption band increases in intensity and shifts to 858 nm.

The same conditions were employed for titration of bis-Zn/Cu **10** (Figure 5). After addition of 1 equivalent of $[\mathrm{Ru(bpy)_3}]^{3+}$, the Q band at $\lambda_{\max} =$ 555 nm decreases while a broad absorption band appears around 617 nm. A new band, characteristic of a radical cation, also exists at $\lambda_{\max} =$ 877 nm. When 2 equivalents of oxidant are added, the Q bands completely disappear. This clearly indicates formation of bis(radical cation) $[\text{bis-Zn/Cu}]^{2+}$. Thus, absorption bands

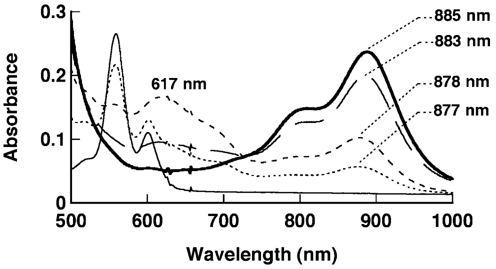


Figure 5. Spectrophotometric titration of bis-Zn/Cu **10** (1.0×10^{-5} м) by $[\mathrm{Ru(bpy)_3}]^{3+}$ (——: bis-Zn/Cu, •••••: $[\text{bis-Zn/Cu}]^{\cdot+}$, -----: $[\text{bis-Zn/Cu}]^{2+}$, – – –: $[\text{bis-Zn/Cu}]^{3+}$, ——: $[\text{bis-Zn/Cu}]^{4+}$) in PhCN at 298 K.

at $\lambda_{max}=615$ and 878 nm increase by a factor of two (Figure 5). After addition of 3 equivalents of $[Ru(bpy)_3]^{3+}$, the band at 615 nm partially decreases, while that at 878 nm increases in intensity and shifts to 883 nm. The resulting spectrum is assigned to trication [bis-Zn/Cu]$^{3+}$. The fully oxidized species [bis-Zn/Cu]$^{4+}$ is finally obtained by adding 4 equivalents of $[Ru(bpy)_3]^{3+}$. The absorption band at $\lambda_{max}=$ 883 nm increases again in intensity and shifts to 885 nm.

Comparing UV/Vis spectra of fully oxidized species [bis-Zn]$^{4+}$ and [bis-Zn/Cu]$^{4+}$ (Figure 6) clearly indicates a red-shift of the absorption bands of [bis-Zn/Cu]$^{4+}$ due to electronic interaction between the two porphyrin units in bis-Zn/Cu **10**. Such an electronic interaction was detected in the oxidized state only for bis-Zn/Cu **10**, in agreement with the conformational change from the open form of bis-Zn **9** to the closed form of bis-Zn/Cu **10**.

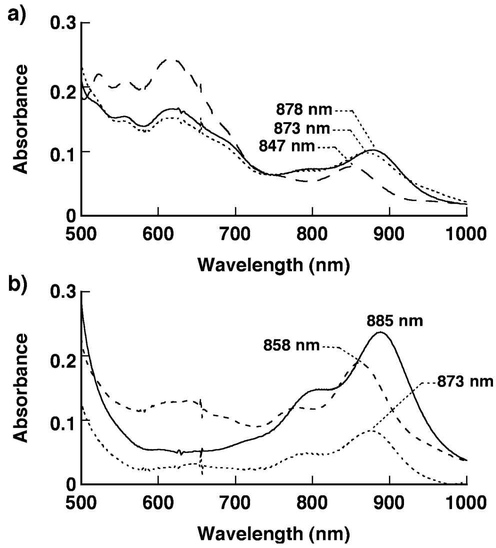


Figure 6. a) Comparison of UV/Vis spectra of [(TpTP)Zn]$^{\cdot+}$ (-----), [bis-Zn]$^{2+}$ (•••••), and [bis-Zn/Cu]$^{2+}$ (——) in PhCN (1×10^{-5} M) at 298 K. b) Comparison of UV/Vis spectra of [(TpTP)Zn]$^{2+}$ (-----), [bis-Zn]$^{4+}$ (•••••), and [bis-Zn/Cu]$^{4+}$ (——) under the same conditions as a).

Dynamics of copper(II) coordination and electron transfer: Spectral titration of bis-Zn **9** by copper(II) triflate (Cu(OTf)$_2$) in CH_2Cl_2/MeOH (1/1; Figure 7) indicates that copper(II) ion is coordinated to the spacer unit stoichiometrically. Coordination of the copper(II) ion to the N-donor unit of bis-Zn **9** is evidenced by the EPR spectrum, which is clearly different from that of Cu(OTf)$_2$, as shown in Figure 8. A decrease in the isotropic g value ($g_0=2.124$ for bis-Zn/Cu and $g_0=2.207$ for Cu(OTf)$_2$) and an increase in the isotropic hyperfine coupling due to copper(II) ion ($A_0=$ 87 G for bis-Zn/Cu and $A_0=38$ G for Cu(OTf)$_2$) observed in Figure 8 are known to result from the stronger equatorial ligand field caused by coordination of copper(II) ion to the N donors of the spacer unit.[42]

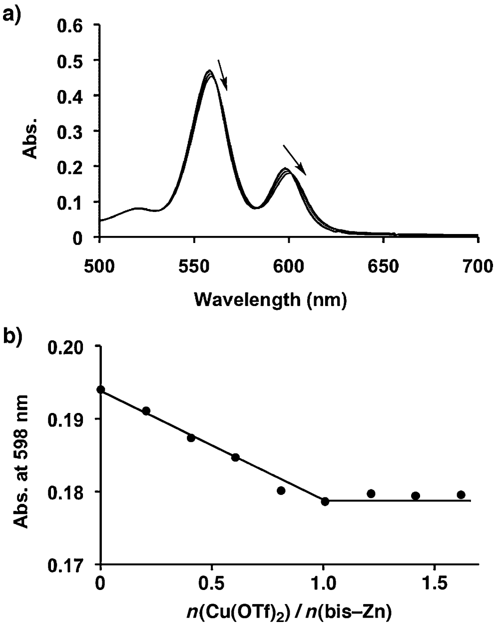


Figure 7. a) UV/Vis spectral titration of bis-Zn 9 (2.2×10^{-5} M) by Cu(OTf)$_2$ in CH_2Cl_2/MeOH (1/1) at 298 K. b) Plot of absorption at 598 nm versus n(Cu(OTf)$_2$)/n(bis-Zn).

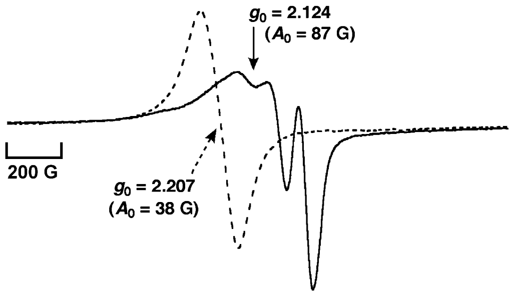


Figure 8. EPR spectra of Cu(OTf)$_2$ (-----) and bis-Zn **9** in the presence of 1 equiv of Cu(OTf)$_2$ (——) in CH_2Cl_2/MeOH (1/1) at 298 K.

Kinetic studies were performed by using a stopped-flow UV/Vis spectroscopic technique. Transient absorption spectra after addition of 10 equivalents of Cu(OTf)$_2$ to bis-Zn **9** are shown in Figure 9a and b. A decrease in intensity and redshift of Q bands at 550 and 598 nm along with increase in intensity at 450 nm due to copper(II) inside the spacer are observed. The same experiments were performed with different amounts of Cu(OTf)$_2$ (Figure 9c), and each decay of the absorbance at 598 nm obeys pseudo-first-order kinetics. From the plot of the observed pseudo-first-order rate constant k_{obs} versus [Cu(OTf)$_2$], the rate constant of coordination of Cu(OTf)$_2$ to bis-Zn in a CH_2Cl_2/MeOH (1/1) at 298 K was determined to be $k_{coord.}=4.0\times10^4\,M^{-1}s^{-1}$.

In PhCN/MeCN (1/1), electron transfer from bis-Zn **9** to Cu(OTf)$_2$ occurs following coordination of copper(II) in bis-Zn **9** (Scheme 5), because the reduction potential of Cu(OTf)$_2$ (Supporting Information Figure S19: peak potential at 0.52 V for Cu^{II}/Cu^{I} vs. Ag/AgNO$_3$ in PhCN/MeCN) is high enough to oxidize bis-Zn **9** and bis-Zn/Cu **10** to dicationic species in PhCN/MeCN.[43–45] Figure 10 shows spectral titration of bis-Zn **9** by Cu(OTf)$_2$ in PhCN/MeCN (1/1). Neither a decrease in absorbance at 558 nm due to neutral porphyrin nor an increase in absorbance at 620 nm due to por-

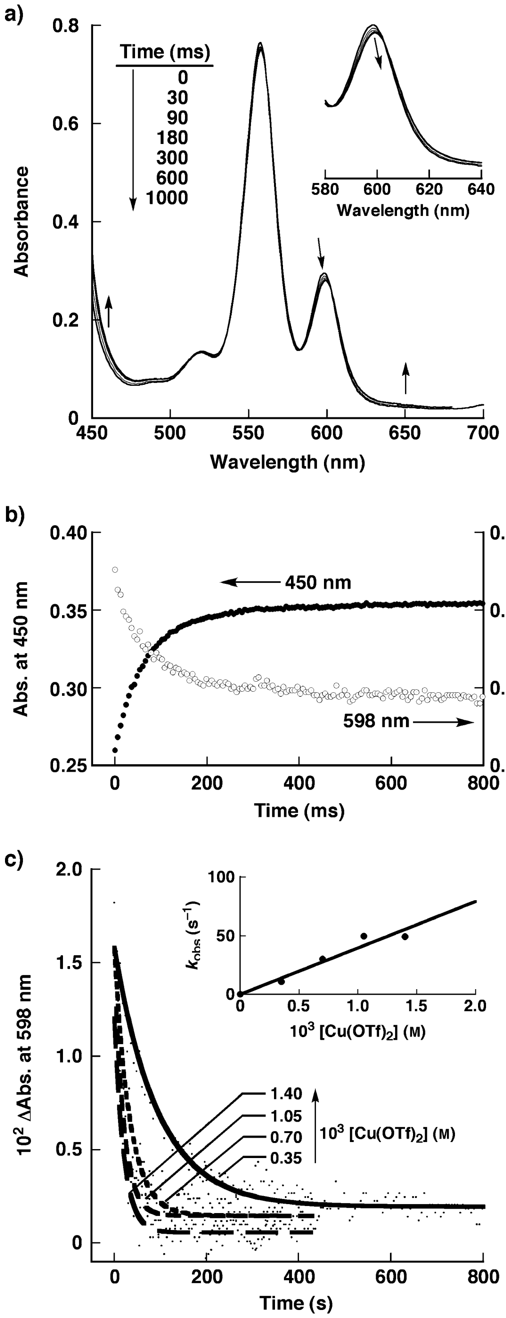
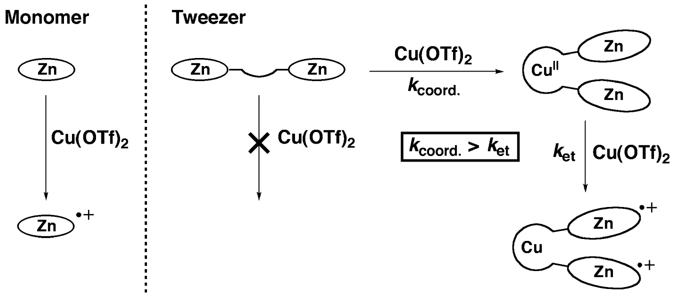


Figure 9. a) UV/Vis spectral changes on adding 10 equiv of Cu(OTf)$_2$ to bis-Zn **9** (3.5×10^{-5} M) in CH_2Cl_2/MeOH (1/1); inset: expanded view of the absorbance at ≈600 nm. b) Absorbance changes at 450 and 598 nm. c) Decay of ΔAbs. at 598 nm for different Cu(OTf)$_2$ concentrations; inset: plot of k_{obs} vs. [Cu(OTf)$_2$].

phyrin radical cation was observed before addition of 1 equivalent of Cu(OTf)$_2$ (Figure 10c). Further addition of Cu(OTf)$_2$ resulted in electron-transfer oxidation of bis-Zn/Cu **10**. The spectrum obtained after addition of 3 equivalents of Cu(OTf)$_2$ agrees with the spectrum of [bis-Zn/Cu]$^{2+}$ (Figure 5). This result indicates that 1:1 stoichiometric coordination between bis-Zn **9** and copper(II) ion occurs prior to electron transfer. In sharp contrast, only the electron-transfer oxidation of the porphyrin ring takes place in case



Scheme 5. Electron transfer from (TpTP)Zn to Cu(OTf)$_2$ (left), and coordination of copper(II) to bis-Zn 9 followed by electron transfer from bis-Zn/Cu to Cu(OTf)$_2$ (right).

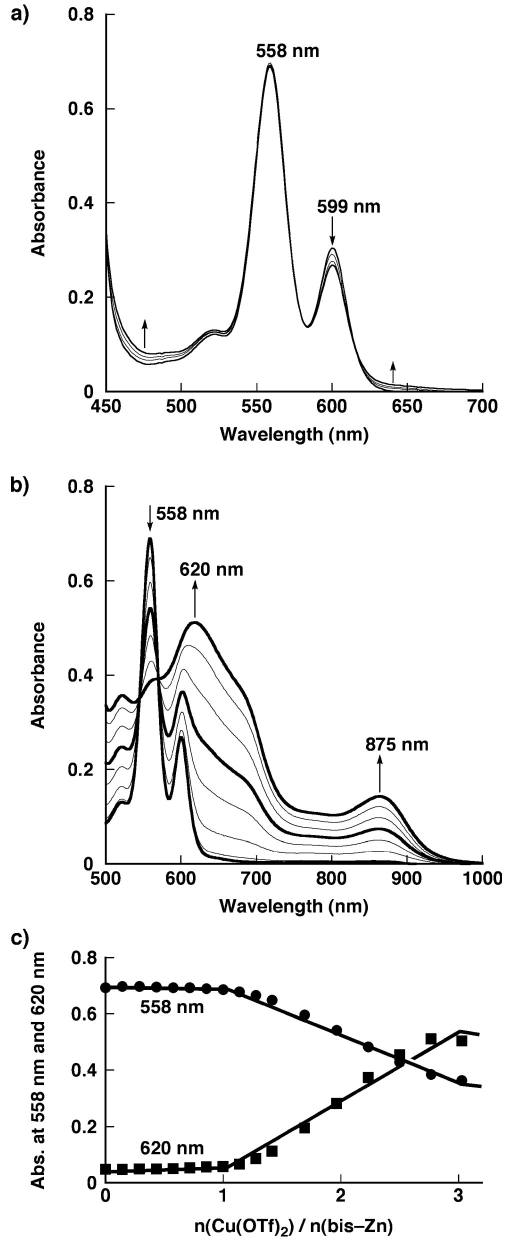


Figure 10. UV/Vis spectral changes of bis-Zn **9** (3.0×10^{-5} M) on addition of Cu(OTf)$_2$. a) 0 to 1 equiv, b) 1 to 3 equiv in PhCN/MeCN (1/1) at 298 K. c) Absorbance (Abs.) changes at 558 and 620 nm.

of (TpTP)Zn on addition of $Cu(OTf)_2$ (Figure S20, Supporting Information). Stoichiometric oxidation of (TpTP)Zn with 1 equivalent of $Cu(OTf)_2$ affords $(TpTP)Zn^{\cdot+}$.

Stopped-flow UV/Vis spectroscopy was used under the same conditions to compare the rate constants of copper(II) coordination to bis-Zn **9** and electron-transfer oxidation of bis-Zn/Cu. The absorption spectrum of bis-Zn **9** changes immediately after addition of 1 equivalent of $Cu(OTf)_2$ due to copper(II) coordination (Figure S21, Supporting Information). From the time profile of the spectral change at 598 nm, the coordination rate constant is estimated to be greater than $10^7\,\text{M}^{-1}\text{s}^{-1}$ in PhCN/MeCN. Once a copper(II) ion is coordinated to bis-Zn **9** to form bis-Zn/Cu, two-electron oxidation of bis-Zn/Cu occurs on the millisecond timescale (Figure 11). The rise and decay at 620 and 558 nm, respectively, obey pseudo-first-order kinetics under the present conditions. The pseudo-first-order rate constant k_{obs} increases linearly with increasing concentration of $Cu(OTf)_2$ to give an electron-transfer rate constant of $k_{et} = 5.3\times10^4\,\text{M}^{-1}\text{s}^{-1}$ (Figure 11c).

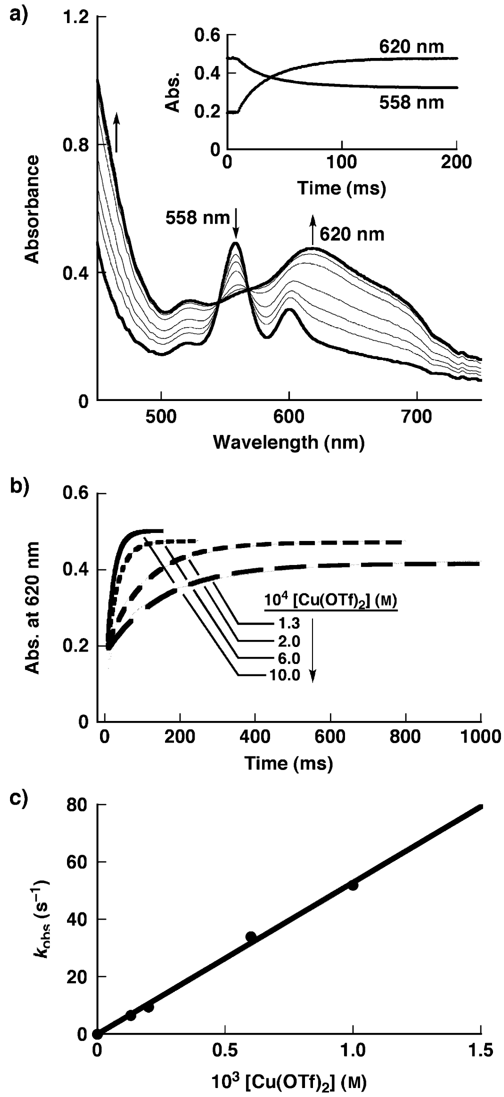


Figure 11. a) UV/Vis spectral changes of bis-Zn/Cu **10** ($2.8\times10^{-5}\,\text{M}$) on addition of $Cu(OTf)_2$ ($6.0\times10^{-4}\,\text{M}$) in a PhCN/MeCN (1:1) mixture; inset: rise and decay at 558 and 620 nm. b) Increase in Abs. at 620 nm for different $Cu(OTf)_2$ concentrations. c) Plot of k_{obs} vs. $[Cu(OTf)_2]$.

Similar experiments were performed for (TpTP)Zn in the presence of an excess of $Cu(OTf)_2$ (Figure S22, Supporting Information). The k_{et} value for (TpTP)Zn was determined to be $6.8\times10^4\,\text{M}^{-1}\text{s}^{-1}$. The slightly faster electron-transfer oxidation of (TpTP)Zn is in accordance with the lower oxidation potential of (TpTP)Zn than that of bis-Zn/Cu (Table 1).

Conclusion

Zinc bis-porphyrin molecular tweezers bis-Zn **9** was obtained by multistep synthesis in high yield. Coordination of a copper(II) ion inside the bridge of the molecular tweezers induced a conformational change of the tweezers from an open to a closed form. The two-electron oxidation potentials of zinc porphyrin radical cations of bis-Zn **9** are split into two one-electron oxidation potentials in the closed form of the tweezers with coordinated copper(II) ion due to electronic communication between porphyrins in the two-electron-oxidized state. The rate constant of coordination of $Cu(OTf)_2$ to bis-Zn **9** was determined to be $k_{coord.} = 4.0\times10^4\,\text{M}^{-1}\text{s}^{-1}$ in CH_2Cl_2/MeOH (1/1) at 298 K. In PhCN/MeCN (1/1), the coordination rate of $Cu(OTf)_2$ to bis-Zn became much faster, with a rate constant exceeding $10^7\,\text{M}^{-1}\text{s}^{-1}$, and subsequent electron transfer from bis-Zn/Cu to $Cu(OTf)_2$ occurred with a rate constant of $5.3\times10^4\,\text{M}^{-1}\text{s}^{-1}$ to afford zinc porphyrin radical cations, which interact with each other in the closed form of the tweezers. Such dynamics of metal-ion coordination and electron transfer which induce conformational changes of complexes provide a new basis for the design of metal complexes whose electronic structure and electron-transfer properties are well controlled by metal-ion coordination.

Experimental Section

Chemicals and reagents: Silica gel (Merck; 70–120 mm) and alumina (Merck; aluminum oxide 90 standardized) were used for column chromatography. Analytical thin layer chromatography was performed on Merck 60 F254 silica gel (precoated sheets, 0.2 mm thick). Reactions were monitored by thin-layer chromatography, UV/Vis spectroscopy, and MALDI/TOF mass spectrometry. $[Ru^{III}(bpy)_3](PF_6)_3$ was prepared from $[Ru^{II}(bpy)_3]Cl_2\cdot6H_2O$ by oxidation with PbO_2.[46] Absolute CH_2Cl_2 (Carlo Erba) and $CHCl_3$ for synthesis and dichloromethane, spectroscopic-grade MeCN (Nacalai Tesque), and 2-MeTHF (Tokyo Chemical Industry Co.) for analysis, were obtained commercially and used without further purification. Benzonitrile was purchased from Wako Pure Chemical Industries and distilled with P_2O_5 under reduced pressure.[47] THF (Acros) and toluene (Aldrich) for reactions were of reagent grade and dried and distilled from sodium/benzophenone under nitrogen immediately before use. Methyl-5-bromopyridine-2-carboxylate is commercially available and was used as received. Zinc(II) tetra-*p*-tolylporphyrin[48] and 5-dihydrodipyrromethane[28] were synthesized as already described.

Physicochemical characterization of compounds: ^{1}H NMR and ^{13}C NMR spectra for synthesized compounds were recorded on a Bruker DRX-300

AVANCE spectrometer and a Bruker DRX-600 AVANCE II spectrometer, respectively, at the Plateforme d'Analyse Chimique et de Synthèse Moléculaire de l'Université de Bourgogne (PACSMUB). Chemical shifts for ^{1}H NMR spectra are expressed in parts per million (ppm) relative to chloroform (7.26 ppm) or [D$_5$]pyridine (7.22, 7.58, and 8.74 ppm). Chemical shifts for ^{13}C NMR spectra are expressed in ppm relative to [D$_5$]pyridine (123.87, 135.91, and 150.35 ppm). The mass spectra were obtained on a Bruker Daltonics Ultraflex II spectrometer at PACSMUB in the MALDI/TOF reflectron mode with dithranol as matrix. High-resolution mass spectra (HRMS) were recorded on a Bruker Daltonics Ultraflex II with polyethylene glycol ion series as internal calibrant or on a Bruker Micro-ToF Q instrument in ESI mode. GC-MS analysis was carried out on a Thermo Trace GC-Ultra-DSQII instrument in EI ionization mode (Thermo TR-5MS nonpolar column, 0.25 mm diameter × 30 m length). Microanalyses were performed on a CHNS/O Analysis Thermo Electron Flash EA 1112 Series.

Photophysical measurements: UV/Vis/NIR spectra were recorded on a Varian Cary 1 spectrophotometer, a Shimadzu UV-3100PC spectrometer, or a Hewlett Packard 8453 diode-array spectrophotometer. Kinetic measurements were performed by using a UNISOKU RSP-601 stopped-flow spectrophotometer with an MOS-type high-sensitivity photodiode array. Pseudo-first-order rate constants were determined by least-squares curve fits.

Electrochemical measurements: Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were carried out with a BAS 100W electrochemical analyzer in a deaerated solvent containing 0.10 M nBu$_4$NPF$_6$ as a supporting electrolyte at 298 K. A conventional three-electrode cell was used with a platinum working electrode and a platinum wire as counterelectrode. The redox potentials were measured with respect to the Ag/AgNO$_3$ (1.0×10^{-2} M) reference electrode. The oxidation potential of ferrocene as external standard is 0.06 V in PhCN.

EPR measurements: The EPR spectra were measured with a JEOL X-band spectrometer (JES-RE1XE). The EPR spectra were recorded under nonsaturating microwave power. The magnitude of the modulation was chosen to optimize the resolution and the signal-to-noise ratio of the observed spectra. The g values were calibrated with an Mn^{2+} marker. PhCN solutions were deaerated by argon purging for 10 min prior to use.

Theoretical calculations: DFT calculations were performed on a 32-processor QuantumCube. Geometry optimizations were carried out with the Becke 3LYP functional and LanL2DZ basis set in Gaussian 09, revision A.02.[49] The graphics were drawn with the Gauss View software program (version 5.0) developed by Semichem.

5,15-Di-*p*-tolylporphyrin (1): *p*-Tolualdehyde (1 mL, 8.45 mmol) and trifluoroacetic acid (0.40 mL, 5.38 mmol) were added to a solution of 5-dihydrodipyrromethane (1.25 g, 8.55 mmol) in degassed CH$_2$Cl$_2$ (1.5 L). Under nitrogen atmosphere, the solution was stirred for 3 h at RT in the dark. After adding tetrachloro-*p*-benzoquinone (TCQ; 3.15 g, 12.81 mmol), the reaction mixture was stirred for three more hours. Triethylamine (3 mL) was added and the reaction mixture was filtered through alumina gel. Compound **1** was eluted with CH$_2$Cl$_2$ and recrystallized from CH$_2$Cl$_2$/MeOH (1.00 g, 49 %). ^{1}H NMR (300 MHz, CDCl$_3$): $\delta=-3.11$ (s, 2H; NH), 2.72 (s, 6H; CH$_3$), 7.61 (d, $^3J=7.7$ Hz, 4H; H$_{m\text{-tolyl}}$), 8.15 (d, $^3J=7.7$ Hz, 4H; H$_{o\text{-tolyl}}$), 9.09 (d, $^3J=4.5$ Hz, 4H; H$_{\beta\text{-pyrr.}}$), 9.37 (d, $^3J=4.5$ Hz, 4H; H$_{\beta\text{-pyrr.}}$), 10.29 ppm (s, 2H; H$_{meso}$); UV/Vis (CH$_2$Cl$_2$): $\lambda_{\max}$ ($10^{-3}\varepsilon$) = 407 (321), 503 (15.1), 538 (6.0), 577 (5.5), 631 nm (2.4 M^{-1}cm^{-1}); MS (MALDI/TOF): m/z calcd for C$_{34}$H$_{27}$N$_4^+$: 491.22; found: 490.86 [M+H]$^+$.

Zinc(II) 5,15-di-*p*-tolyl-10-phenylporphyrin (2): 5,15-*p*-Tolylporphyrin **1** (89.8 mg, 0.18 mmol) was dissolved in CHCl$_3$ (100 mL), and a solution of zinc(II) acetate dihydrate (80.4 mg, 0.37 mmol) and anhydrous sodium acetate (61.0 mg, 0.74 mmol) in MeOH (100 mL) was added. After 2 h at reflux, the reaction mixture was cooled to RT. The organic layer was washed three times with a solution of water saturated in sodium bicarbonate, dried over magnesium sulfate, and the solvent evaporated. The crude product was purified by column chromatography over silica gel (CH$_2$Cl$_2$), affording the metalated porphyrin (100.4 mg, 0.18 mmol). This was then dissolved in distilled and degassed THF (55 mL). Under argon, the reaction mixture was cooled to 0 °C before adding dropwise a solution of phenyllithium (2 M, 0.54 mL, 1.08 mmol). After 15 min of stirring at 0 °C and 15 min of stirring at RT, water/THF (10 %, 10 mL) was carefully added. The reaction mixture was stirred for 10 min at RT and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ; 164.2 mg, 0.72 mmol) was added. After 1 h, the reaction mixture was filtered over alumina gel (CH$_2$Cl$_2$) and column chromatography over alumina gel (heptane/CH$_2$Cl$_2$ 3/1) gave **2** (79.2 mg, 70 %). ^{1}H NMR (300 MHz, CDCl$_3$): $\delta=2.73$ (s, 6H; CH$_3$), 7.57 (d, $^3J=7.7$ Hz, 4H; H$_{m\text{-tolyl}}$), 7.74 (d, $^3J=7.6$ Hz, 2H; H$_{m\text{-phenyl}}$), 7.75 (dd, $^3J_1={}^3J_2=7.6$ Hz, 1H; H$_{p\text{-phenyl}}$), 8.09 (d, $^3J=7.7$ Hz, 4H; H$_{o\text{-tolyl}}$), 8.21 (dd, $^3J_1=7.6$ Hz, $^3J_2=1.6$ Hz, 2H; H$_{o\text{-phenyl}}$), 8.95 (d, $^3J=4.5$ Hz, 2H; H$_{\beta\text{-pyrr.}}$), 9.00 (d, $^3J=4.5$ Hz, 2H; H$_{\beta\text{-pyrr.}}$), 9.01 (d, $^3J=4.5$ Hz, 2H; H$_{\beta\text{-pyrr.}}$), 9.21 (d, $^3J=4.5$ Hz, 2H; H$_{\beta\text{-pyrr.}}$), 9.99 ppm (s, 1H; H$_{meso}$); UV/Vis (CH$_2$Cl$_2$): $\lambda_{\max}$ ($10^{-3}\varepsilon$) = 415 (471), 544 (18.7), 581 nm (2.7 M^{-1}cm^{-1}); MS (MALDI/TOF): m/z calcd for C$_{40}$H$_{29}$N$_4$Zn$^+$: 629.17; found: 628.90 [M+H]$^+$.

Zinc(II) 5,15-*p*-tolyl-10-phenyl-20-bromoporphyrin (3): Zinc(II) 5,15-*p*-tolyl-10-phenylporphyrin **2** (140.3 mg, 0.223 mmol) was dissolved in CH$_2$Cl$_2$ (220 mL) and cooled to 0 °C. After adding two drops of pyridine and recrystallized *N*-bromosuccinimide (43.8 mg, 0.246 mmol), reaction mixture was stirred for 30 min at 0 °C. Then, reaction was quenched by acetone (11 mL). The organic layer was washed three times with distilled water, dried over magnesium sulfate, and the solvent evaporated. The crude product was purified by column chromatography over silica gel (CH$_2$Cl$_2$), affording the porphyrin **3** (142.1 mg, 90 %). The ^{1}H NMR spectrum of free base **3′** was measured after demetalation of **3**. ^{1}H NMR of **3′** (300 MHz, CDCl$_3$): $\delta=-2.74$ (s, 2H; NH), 2.71 (s, 6H; CH$_3$), 7.55 (d, $^3J=7.7$ Hz, 4H; H$_{m\text{-tolyl}}$), 7.73 (d, $^3J=7.6$ Hz, 2H; H$_{m\text{-phenyl}}$), 7.74 (dd, $^3J_1={}^3J_2=7.6$ Hz, 1H; H$_{p\text{-phenyl}}$), 8.06 (d, $^3J=7.7$ Hz, 4H; H$_{o\text{-tolyl}}$), 8.18 (dd, $^3J_1=7.6$ Hz, $^4J_2=1.6$ Hz, 2H; H$_{o\text{-phenyl}}$), 8.78 (d, $^3J=4.5$ Hz, 2H; H$_{\beta\text{-pyrr.}}$), 9.82 (d, $^3J=4.5$ Hz, 2H; H$_{\beta\text{-pyrr.}}$), 8.91 (d, $^3J=4.5$ Hz, 2H; H$_{\beta\text{-pyrr.}}$), 9.64 ppm (d, $^3J=4.5$ Hz, 2H; H$_{\beta\text{-pyrr.}}$); UV/Vis (CH$_2$Cl$_2$): $\lambda_{\max}$ ($10^{-3}\varepsilon$) = 423 (446), 555 (16.7), 597 nm (5.6 M^{-1}cm^{-1}); MS (MALDI/TOF): m/z calcd for C$_{40}$H$_{28}$BrN$_4$Zn$^+$: 707.08; found: 706.86 [M+H]$^+$.

Zinc(II) 5,15-di-*p*-tolyl-10-phenyl-20-[4′,4′,5′,5′-tetramethyl-(1′,2′,3′dioxaborolan-2′-yl)]porphyrin (4): Under nitrogen atmosphere, triethylamine (0.32 mL, 2.30 mmol), *trans*-[PdCl$_2$(PPh$_3$)] (3.8 mg, 0.005 mmol), pinacolborane (0.21 mL, 1.45 mmol), and **3** (124.1 mg, 0.18 mmol) were dissolved in 1,2-dichloroethane (20 mL) dried over molecular sieves. After 1 h at reflux, the reaction mixture was cooled to RT. The reaction was quenched by adding an aqueous solution of KCl (30 %, 7 mL) and the product extracted with CH$_2$Cl$_2$ (100 mL). The organic layer was washed three times with distilled water, dried over magnesium sulfate, and the solvent evaporated. The crude product was purified by column chromatography over silica gel (CH$_2$Cl$_2$/heptane 1/1), affording porphyrin **4** (131.9 mg, 99 %). ^{1}H NMR (300 MHz, CDCl$_3$): $\delta=1.85$ (s, 12H; CH$_3$), 2.71 (s, 6H; PhC*H$_3$*), 7.55 (d, $^3J=7.7$ Hz, 4H; H$_{m\text{-tolyl}}$), 7.73 (d, $^3J=7.6$ Hz, 2H; H$_{m\text{-phenyl}}$), 7.74 (dd, $^3J_1={}^3J_2=7.6$ Hz, 1H; H$_{p\text{-phenyl}}$), 8.10 (d, $^3J=7.7$ Hz, 4H; H$_{o\text{-tolyl}}$), 8.20 (dd, $^3J_1=7.6$ Hz, $^4J_2=1.6$ Hz, 2H; H$_{o\text{-phenyl}}$), 8.94 (d, $^3J=4.5$ Hz, 2H; H$_{\beta\text{-pyrr.}}$), 9.82 (d, $^3J=4.5$ Hz, 2H; H$_{\beta\text{-pyrr.}}$), 9.10 (d, $^3J=4.5$ Hz, 2H; H$_{\beta\text{-pyrr.}}$), 9.90 ppm (d, $^3J=4.5$ Hz, 2H; H$_{\beta\text{-pyrr.}}$); UV/Vis (CH$_2$Cl$_2$): $\lambda_{\max}$ ($10^{-3}\varepsilon$) = 418 (366), 548 (13.1), 584 nm (1.4 M^{-1}cm^{-1}); MS (MALDI/TOF): m/z calcd for C$_{40}$H$_{40}$BN$_4$O$_2$Zn$^+$: 755.25; found: 755.22 [M+H]$^+$.

2-Bromo-2-hydroxymethylpyridine (5):[50] A solution of ethyl 5-bromopyridine-2-carboxylate (1.00 g, 4.63 mmol) in MeOH (20 mL) was cooled to 0 °C. Sodium borohydride (0.92 g, 24.33 mmol) was added portionwise. After 4 h of stirring at RT, the solvent was evaporated. Then, distilled water was added and the product extracted with CH$_2$Cl$_2$. The organic layer was washed two times with distilled water, dried over magnesium sulfate and the solvent evaporated to afford **5** (0.58 g, 67 %) without any purification. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta=4.74$ (s, 2H; C*H$_2$*OH), 4.89 (s, 1H; OH), 7.21 (d, $^3J=8.2$ Hz, 1H; H3), 7.83 (dd, $^3J_1=8.2$ Hz, $^4J_2=1.5$ Hz, 1H; H4), 8.63 ppm (d, $^4J=1.5$ Hz, 1H; H6); GC-MS (EI, 70 eV): m/z calcd for C$_6$H$_6$BrNO$^+$: 187.0; found: 187.0 (8) [M]$^+$; m/z calcd for C$_5$H$_4$BrN$^+$: 157.0; found: 157.0 (15) [$M-$CH$_2$OH]$^+$.

2-Chloromethyl-5-bromopyridine (6):[51] Compound **5** (1.61 g, 8.56 mmol) was dissolved in toluene (40 mL). Thionyl chloride (1.9 mL, 26.19 mmol) was added dropwise. After 3 h of stirring at RT, the reaction mixture was quenched by addition of an aqueous solution saturated with sodium bicarbonate. The crude product was extracted three times with $\mathrm{CH_2Cl_2}$. The organic layer was dried over magnesium sulfate and the solvent evaporated to give **6** (1.48 g, 84 %) without any purification. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 4.67$ (s, 2H; $\mathrm{C}\mathit{H}_2\mathrm{Cl}$), 7.43 (d, $^3J = 8.2$ Hz, 1H; H3), 7.90 (dd, $^3J_1 = 8.2$ Hz, $^4J_2 = 2.2$ Hz, 1H; H4), 8.64 ppm (d, $^4J = 2.2$ Hz, 1H; H6); GC-MS (EI, 70 eV): *m/z* calcd for $\mathrm{C_6H_5ClBrN^+}$: 204.9; found: 204.9 (38) $[M]^+$; *m/z* calcd for $\mathrm{C_6H_5BrN^+}$: 170.0; found: 169.9 (60) $[M-\mathrm{Cl}]^+$.

***N,N′*-Bis[(5-bromopyrid-2-yl)methyl]-*N,N′*-dimethylpropane-1,3-diamine (7)**: Potassium carbonate (3.6 g, 26.05 mmol) was introduced into a three-neck round-bottom flask. After three vacuum/argon cycles, **6** (1.34 g, 6.49 mmol) and *N,N′*-dimethylpropane-1,3-diamine (0.47 mL, 3.24 mmol) dissolved in acetonitrile (90 mL) were added. After three days of stirring at RT, the crude product was extracted with $\mathrm{CH_2Cl_2}$. The organic layer was washed three times with distilled water, dried over magnesium sulfate, and the solvent evaporated at 40 °C to obtain **7** (1.42 g, 99 %) without any purification. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 1.65$ (qt, $^3J = 7.0$ Hz, 2H; $\mathrm{CH_2}\mathit{CH}_2\mathrm{CH_2}$), 2.15 (s, 6H; $\mathrm{CH_3}$), 2.37 (t, $^3J = 7.0$ Hz, 4H; $\mathit{CH}_2\mathrm{CH_2}\mathit{CH}_2$), 3.50 (s, 4H; $\mathit{CH}_2\mathrm{Py}$), 7.21 (d, $^3J = 8.2$ Hz, 2H; H3), 7.67 (dd, $^3J_1 = 8.2$ Hz, $^4J_2 = 2.2$ Hz, 2H; H4), 8.50 ppm (d, $^4J = 2.2$ Hz, 2H; H6); MS: compound **7** could not be characterized by mass spectrometry due to its instability.

***N,N′*-Bis[({5-[zinc(II) 5,15-*p*-tolyl-10-phenylporphyrin]}pyrid-2-yl)-methyl]-*N,N′*-dimethylpropane-1,3-diamine (9)**: Sodium iodide (0.24 g, 1.60 mmol), cesium(I) carbonate (1.61 g, 4,94 mmol), $[\{\mathrm{PdCl}(\eta^3\text{-}\mathrm{C_3H_5})\}_2]$ (57.3 mg, 0.16 mmol), and triphenylphosphine (169.9 mg, 0.65 mmol) were introduced into a three-neck round-bottom flask. After three vacuum/argon cycles, DMF (90 mL) dried over molecular sieves and distilled toluene (150 mL) containing **7** (0.73 g, 1.65 mmol) were added. The reaction mixture was heated at 80 °C for 12 h before addition of **4** (1.21 g, 1.60 mmol) in distilled toluene (50 mL). The reaction mixture was then heated to reflux for a further 12 h at 80 °C. After cooling to RT, the organic layer was washed three times with an aqueous solution saturated with sodium bicarbonate, dried over magnesium sulfate, and the solvent evaporated. The crude product was purified by column chromatography over silica gel neutralized by adding triethylamine (eluent: $\mathrm{CH_2Cl_2}$ then $\mathrm{CH_2Cl_2/EtOH/NH_3}$ (25 % in water) 80/20/1) to obtain **9** (634.3 mg, 52 %). ^{1}H NMR (300 MHz, $[\mathrm{D_5}]$pyridine): $\delta = 2.04$ (qt, $^3J = 7.0$ Hz, 2H; $\mathrm{CH_2}\mathit{CH}_2\mathrm{CH_2}$), 2.40 (s, 12H; $\mathrm{Ph}\mathit{CH}_3$), 2.51 (s, 6H; $\mathrm{NCH_3}$), 2.84 (t, $^3J = 7.0$ Hz, 4H; $\mathit{CH}_2\mathrm{CH_2}\mathit{CH}_2$), 4.18 (s, 4H; $\mathit{CH}_2\mathrm{Py}$), 7.33 (d, $^3J = 7.7$ Hz, 8H; $\mathrm{H}_{m\text{-tolyl}}$), 7.64 (d, $^3J = 5.2$ Hz, 4H; $\mathrm{H}_{m\text{-phenyl}}$), 7.65 (dd, $^3J_1 = {}^3J_2 = 5.2$ Hz, 2H; $\mathrm{H}_{p\text{-phenyl}}$), 8.04 (d, $^3J = 7.7$ Hz, 2H; H3), 8.11 (dd, $^3J_1 = {}^3J_2 = 5.4$ Hz, 8H; $\mathrm{H}_{o\text{-tolyl}}$), 8.27 (dd, $^3J_1 = 5.4$ Hz, $^4J_2 = 1.5$ Hz, 4H; $\mathrm{H}_{o\text{-phenyl}}$), 8.64 (dd, $^3J_1 = 8.2$ Hz, $^4J_2 = 2.2$ Hz, 2H; H4), 9.04 (d, $^3J = 4.5$ Hz, 4H; $\mathrm{H}_{\beta\text{-pyrr.}}$), 9.08 (d, $^3J = 4.5$ Hz, 8H; $\mathrm{H}_{\beta\text{-pyrr.}}$), 9.10 (d, $^3J = 4.5$ Hz, 4H; $\mathrm{H}_{\beta\text{-pyrr.}}$), 9.64 ppm (d, $^4J = 2.2$ Hz, 2H; H6); ^{13}C DEPT-135 NMR (150 MHz, $[\mathrm{D_5}]$pyridine): $\delta = 22.0$ (4 $\mathrm{Ph}\mathit{C}\mathrm{H_3}$), 26.5 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2CH_2}$), 43.1–43.5 (2 $\mathrm{NCH_3}$), 56.1–56.4 ($\mathit{C}\mathrm{H_2CH_2}\mathit{C}\mathrm{H_2}$), 64.2–65.0 (2 $\mathit{C}\mathrm{H_2Py}$), 117.7 (2 C_{meso}), 119.7 (2 C_{meso}), 121.8 (2 $\mathrm{CH_{py}}$), 122.2 (4 C_{meso}), 127.5 (6 $\mathrm{CH_{phenyl}}$), 128.3 (8 $\mathrm{CH_{tolyl}}$), 132.3–133.4 (16 $\mathrm{CH}_{\text{®-pyrr.}}$), 135.6 (8 $\mathrm{CH_{tolyl}}$ + 4 $\mathrm{CH_{phenyl}}$), 137.8 (4 $\mathrm{C_{tolyl}}$), 138.3 (2 $\mathrm{C_{phenyl}}$), 139.7 (2 $\mathrm{CH_{py}}$), 141.4 (4 $\mathrm{C_{tolyl}}$), 144.4 (2 $\mathrm{C_{py}}$), 151.2–151.6 (16 $\mathrm{C_{pyrr.}}$), 154.0 (2 $\mathrm{CH_{py}}$), 160.1 ppm (2 $\mathrm{C_{py}}$); UV/Vis ($\mathrm{CH_2Cl_2}$): $\lambda_{\max}$ ($10^{-3}\varepsilon$) = 421 (655), 551 (22.4), 603 nm (8.7 $\mathrm{M^{-1}cm^{-1}}$); MS (MALDI/TOF): *m/z* calcd for $\mathrm{C_{97}H_{77}N_{12}Zn_2{}^+}$: 1537.50; found: 1537.40 $[M+\mathrm{H}]^+$; HRMS (ESI/TOF): *m/z* calcd for $\mathrm{C_{97}H_{77}N_{12}Zn_2{}^+}$: 1537.4972; found: 1537.4814 $[M+\mathrm{H}]^+$; elemental analysis calcd (%) for $\mathrm{C_{97}H_{76}N_{12}Zn_2{\cdot}CH_2Cl_2{\cdot}2\,EtOH{\cdot}2\,NH_3}$: C 69.94, H 5.52, N 11.19; found: C 69.93, H 5.75, N 11.13.

***N,N′*-Bis[({5-[zinc(II) 5,15-*p*-tolyl-10-phenylporphyrin]}-pyrid-2-yl)-methyl]-*N,N′*-dimethylpropane-1,3-diamine copper(II) (10)**: A solution of MeOH (5 mL) containing copper(II) acetate monohydrate (31.1 mg, 0.156 mmol) was added to a solution of **9** (53.0 mg, 0.034 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL). The reaction mixture was stirred for 5 min at RT. Then the crude product was extracted with $\mathrm{CH_2Cl_2}$ and the organic layer washed three times with distilled water, dried over magnesium sulfate, and the solvent evaporated. Purification by column chromatography over silica gel neutralized by adding triethylamine (eluent: $\mathrm{CH_2Cl_2}$ then $\mathrm{CH_2Cl_2/EtOH/NH_3}$ (25 % in water) 80/20/1) and recrystallization from $\mathrm{CH_2Cl_2/MeOH}$ yielded **10** (38.6 mg, 65 %);.UV/Vis ($\mathrm{CH_2Cl_2}$): $\lambda_{\max}$ ($10^{-3}\varepsilon$) = 422 (639), 551 (26.2), 606 nm (6.8 $\mathrm{M^{-1}cm^{-1}}$); MS (MALDI/TOF): *m/z* calcd for $\mathrm{C_{97}H_{76}CuN_{12}Zn_2{}^+}$: 1599.42; found: 1599.40 $[M-2\,\mathrm{OAc}]^+$; HR-MS (ESI/TOF) *m/z* calcd for $\mathrm{C_{97}H_{76}CuN_{12}Zn_2{}^+}$: 1599.4189; found: 1599.4124 $[M-2\,\mathrm{OAc}]^+$.

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[33] The same absorption maxima are also observed for mono-pyridyl-substituted porphyrins. This indicates that a single pyridyl group scarcely affects the electronic structure of porphyrins.[24]

[34] The open form of bis-Zn **9** (Figure 2a) was always obtained as the optimized structure even when the calculation started from the closed structure. The heat of formation for the open form of bis-Zn **9** is more negative by 40 kcal than that of the closed form, according to single-point energy calculation.

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[37] The peak-to-peak separations of redox waves for bis-Zn/Cu **10** in Figure 3c are 110, 130, and 120 mV. These values are slightly larger than those of ferrocene and (TpTP)Zn (80 mV). Nevertheless, the cyclic voltammograms clearly exhibit three pairs of redox waves.

[38] The current intensity at 1.03 V seems larger than that of the third oxidation process of the porphyrin units at 0.67 V, because one-electron oxidation of the Cu^{II}-coordinated spacer (1.04 V) overlaps, as shown in Figure S14a and S14b of the Supporting Information. Similarly, the broadened redox wave of bis-Zn 9 at around 0.68 V is due to overlap of the oxidation process of the pristine spacer unit (Figure S14c, Supporting Information).

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[40] Spectroelectrochemistry was also performed on bis-Zn **9** in PhCN containing 0.1 M $n\mathrm{Bu_4NPF_6}$ as supporting electrolyte. The UV/Vis/NIR spectral changes are shown in Figure S17 of the Supporting Information.

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[43] The oxidation potential of the porphyrin is more positively shifted in CH_2Cl_2/MeOH due to destabilization of the oxidized states of the

porphyrin in nonpolar solvent, such as CH_2Cl_2, which also hamper electron transfer from porphyrin to $Cu(OTf)_2$.

[44] PhCN/MeCN (1/1) was used because of the solubility of $Cu(OTf)_2$ and bis-Zn **9**.

[45] The copper(I) ion that is formed after electron transfer from porphyrin to copper may be immediately consumed by dioxygen in a cuvette.

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