Synthesis of Bipyridylene-Bridged Bisporphyrin by Nickel-Mediated Coupling Reaction: ON−OFF Control of Cofacial Porphyrin Unit by Reversible Complexation

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Novel bipyridylene-bridged bisporphyrin **1a**, in which two porphyrin units were attached directly to symmetrical 4,4′-positions of the 2,2′-bipyridyl group, was synthesized by a nickel(0)-mediated homocoupling reaction of 5,10,15-tris(*n*-heptyl)-20-(2′-bromo-4′-pyridyl)porphyrinatozinc (**3a**) in 58% yield. Spatial geometries of two porphyrins in **1a** were regulated by reversible complexation of the bipyridyl part with $PdCl_2$. Thus, the addition of 2.2 equiv of palladium chloride to **1a** converted the freely rotating conformation to the cofacial bisporphyrin **2a**. The subsequent addition of 4,4′-dimethyl-2,2′-bipyridine **9** regenerated the initial bisporphyrin **1a**.

Introduction

Cofacial bisporphyrins are interesting molecular tools in various research fields, especially, supramolecular chemistry and materials science.[1] Placement of two porphyrin units in a proximity can be expected to produce characteristic functions such as efficient energy transfer,[2] cooperative molecular recognition,[3] and multielectron activation of small molecules.[4] Since their properties depend much on their mutual geometries and distances, various units to link two porphyrins have been proposed. If external signals or ligands control the relative positions of two porphyrins, these properties can now be controlled on demand. Such a bisporphyrin is applicable as a molecular switch[5] and of use in molecular devices and molecular machines.[6] Here, a molecular unit attached to porphyrin was designed to control the relative orientation of two porphyrins. For this purpose, two porphyrin units were connected directly to symmetrical 4,4′-positions of the bipyridyl group to afford **1**. Since bipyridyl groups are known as strong ligands toward various transition metal ions, the relative position of two porphyrins can be controlled by the addition/elimination equilibrium of metal ions even in dilute concentrations less than the μM scale. Normally, two porphyrins can rotate freely upon the bond connecting two pyridines. Complexation at the bipyridyl part switches the orientation of two porphyrin units to the same side with a dihedral angle of 60° (Scheme 1). In this paper, we report a facile synthesis of **1a** by nickel-mediated coupling reaction of bromopyridinylporphyrin **3a**. Complexation of **1a** with palladium chloride and subsequent removal of the palladium unit with 4,4′-dimethyl-2,2′-bipyridine were also described.

Results and Discussion

In our search for a simple and efficient strategy for the synthesis of bisporphyrin **1**, the first attempt (Scheme 2), consisting of a one-step introduction of two porphyrin units by condensation of 4,4′-diformyl-2,2′-bipyridine and octanal with the alkyl dipyrromethane **4a**, was unsuccessful, as the desired bisporphyrin was identifiable only as a trace component by a MALDI-TOF mass spectrometry and TLC analysis. A homocoupling reaction of bromopyridinylporphyrin **3a** was next examined (Scheme 3). Nickel(0)-mediated coupling reaction of aryl halide normally proceeds under mild conditions, and many successful preparative examples of biaryl compounds

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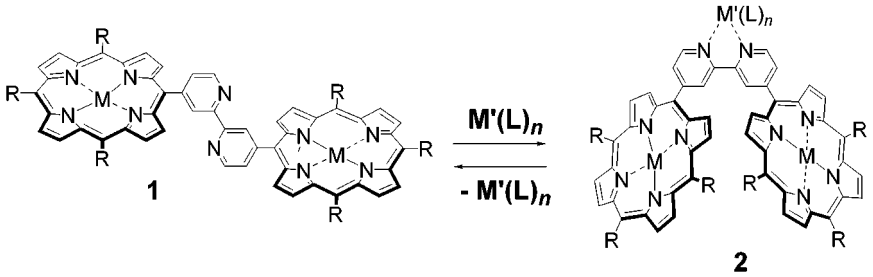
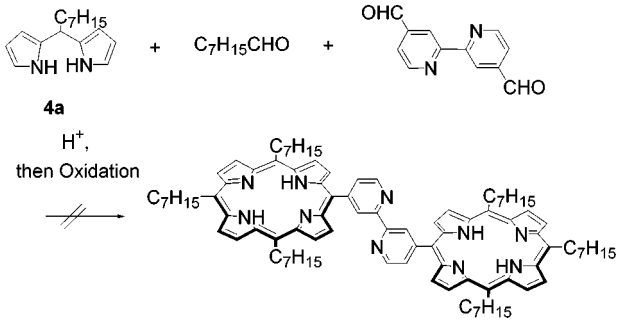
Scheme 1



Scheme 2



have been reported.[7] To the best of our knowledge, however, no synthesis of porphyrin derivatives by nickel(0)-mediated homocoupling reaction has been reported.[8] The precursor **3a** for the coupling was synthesized as shown in Scheme 3. Reaction of 2-bromopyridine-4-aldehyde, octanal, and dipyrromethane **4a** in the presence of CF_3CO_2H (TFA), followed by oxidation with chloranil gave free base porphyrin **5a** in a 12% yield. Treatment of free base porphyrin **5a** with $Zn(OAc)_2$ gave zinc porphyrin **3a** in an 88% yield. Then, the coupling reaction was undertaken according to the procedure reported by Semmelhack.[7a] A mixture of bromopyridylporphyrin **3a** and $Ni(cod)_2$ (0.7 equiv) was stirred at 70 °C in dry DMF, and the progress of reaction was monitored by a MALDI-TOF mass spectrometer. The reaction almost stopped after 24 h, when the crude product was found to contain, besides the desired bipyridylene-bridged bisporphyrin **1a**, significant amounts of the starting material **3a**, debrominated byproduct **6a** and its free base form **7a**.[9] The reaction was optimized by varying the conditions, including the amount of $Ni(cod)_2$ and other additives, the concentration, and the temperature. Theoretically, 0.5 equiv of Ni(0) species should be enough for the coupling of 1 equiv of aryl halide, but an excess amount of $Ni(cod)_2$ was required to consume all the starting material **3a**. Concentration of the aryl halide was also found to be an important factor. While nickel-mediated or -catalyzed coupling reactions of simple aryl halides proceed at relatively high concentrations of reagents (0.2∼0.1 M),[7] the coupling of **3a** required more dilute conditions. The best result was obtained finally by the use of a large excess of $Ni(cod)_2$ (ca. 25 equiv) in the presence of 2,2′-bipyridyl (1.3 equiv) and cyclooctadiene (ca. 30 equiv) with use of 6.6×10^{-4} M **3a** in dry DMF. The starting material **3a** was completely consumed within 24 h, yielding the desired bisporphyrin **1a** as the major product and the debrominated mono-porphyrin **6a** as the byproduct. A detailed reaction mechanism is not clear, but the result suggests the following pathway. Under dilute conditions with use of excess amounts of $Ni(cod)_2$, bromide **3a** must be smoothly converted into pyridylnickelbromide complex.[10] Then, they react intermolecularly to give bispyridylnickel compound and nickel bromide.[11] Finally, the coupling product **1a** is produced by reductive elimination of bispyridylnickel compound.[12] Quick consumption of bromide **3a** seems to be important to prevent production of **6a** and **7a** and proceed with the coupling reaction. After gel permeation chromatography, pure **1a** was isolated in 58% yield. The presence of axial coordination with two molecules of pyridine (from eluent) was consistent with NMR data.

The proton NMR spectrum of **1a** (20 μM in $(CDCl_2)_2$) was shown in Figure 1A. Although bipyridyl signals partly overlapped on β-protons of the porphyrin ring protons, H_3, H_5, and H_6 could be assigned as peaks at 9.6, 8.2, and 9.1 ppm, respectively, by $^1H-^1H$ COSY and TOCSY spectra. Protons of the axial pyridines (PyH_2, PyH_3, and PyH_4) were significantly shielded by the porphyrin and appeared at 3.5, 5.8, and 6.6 ppm, respectively. The shift behavior of pyridine is consistent with previous observations.[13]

The effect of the environment surrounding the porphyrin moieties on the complexation behavior of **1a** was monitored by NMR spectrometry as shown in Figure 1. Solutions of **1a** in $(CDCl_2)_2$ were prepared in NMR sample tubes at two concentrations: (A) 20 μM and (B) 1.6 μM. The spectra were different. In the more dilute solution (B), signals of axial pyridine, especially PyH_2, became unclear by peak broadening based on fast exchange between free and coordinated pyridines. Upon addition of 1.1 equiv of $PdCl_2(CH_3CN)_2$ to sample B, new signals appeared at 9.9, 9.5, 8.8, 8.5, 7.8, 7.3, 4.8, and 2.4 ppm (indicated as arrows in Figure 1C), and signals of **1a** (9.6, 9.0, 8.1, 5.0, and 2.5 ppm) gradually diminished (Figure 1C). After the addition of 2.2 equiv of $PdCl_2(CH_3CN)_2$, palladium complex **2a** was completely formed along with $PdCl_2$(pyridine)$_2$ complex **8** (Figure 1D). Three signals (at

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(9) Ratio of peak-height values of **1a** (including **1a**−Ni complex), **3a**, **6a**, and **7a** in the MALDI-TOF mass spectrum is about 5:3:2:1 after 24 h.

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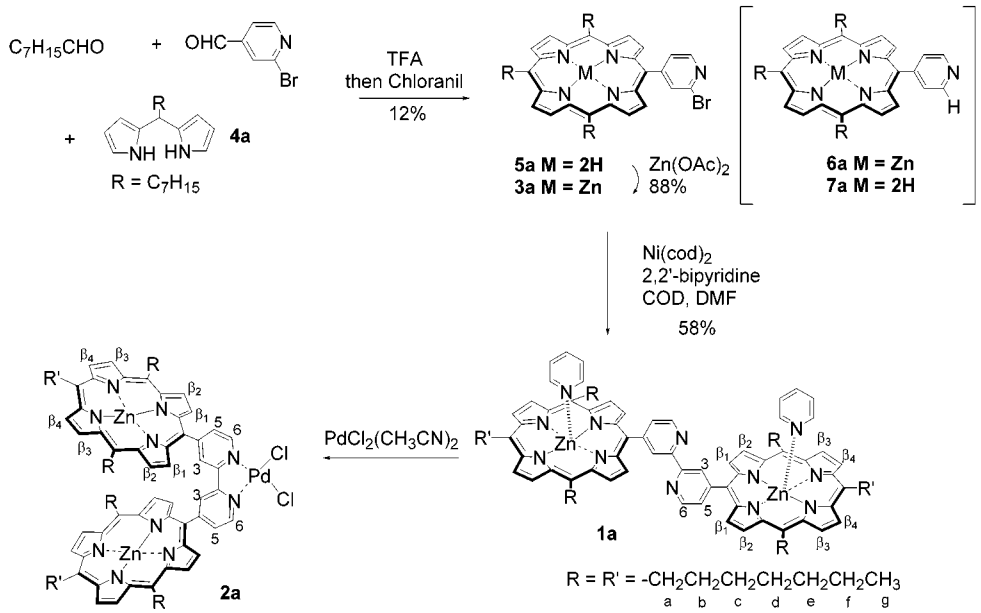
Scheme 3



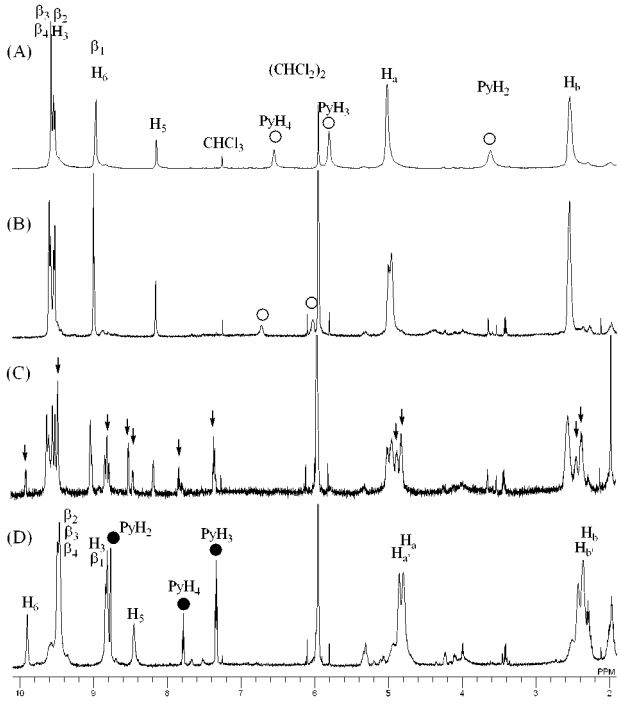


Figure 1. ^{1}H NMR titration of **1a** with $PdCl_2$ (600 MHz, $(CDCl_2)_2$). (A) **1a** (20 μM). (B) **1a** (1.6 μM). (C) B + 1.1 equiv $PdCl_2(CH_3CN)_2$. (D) B + 2.2 equiv $PdCl_2(CH_3CN)_2$ = **2a** + **8**. (○) Coordinated pyridine, (●) $PdCl_2$(pyridine)$_2$ **8**.

8.8 (d, 2H), 7.8 (t, 1H), and 7.3 (t, 2H)) were assigned to **8** by comparison with the authentic sample prepared independently.[14]

To assign signals of **2a** in Figure 1D, a TOCSY NMR spectrum was obtained (Figure 2). Three protons (at 9.9, 8.8 (overlapped with β proton), and 8.4 ppm) were correlated to one another by ^3J and long-range coupling in ^{1}H−^{1}H COSY (spectrum is not shown) and TOCSY spectra. They were assigned as H_6, H_3, and H_5 on the

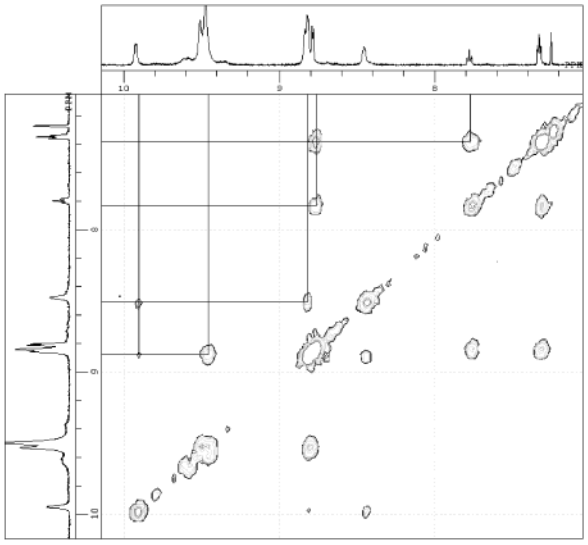


Figure 2. A TOCSY spectrum of **2a** (the same sample of Figure 1D); spin lock time, 0.1 s.

bipyridyl moiety. The large downfield shift of H_6 (+0.9 ppm) reflects the development of δ+ charge upon complexation with $PdCl_2$. On the other hand, H_3 and β-protons moved to upper fields upon complexation in varying degrees. The most sensitive shielding effect of the porphyrin ring current appeared at the H_3 proton (−0.6 ppm). Another change in the ^{1}H NMR spectrum was observed at the alkyl chain parts. According to the symmetry, there are two sets of meso-heptyl groups in porphyrin **1a**, namely, the four R groups adjacent to, and the two R′ groups opposite to, the bipyridyl groups, respectively. Before complexation, however, they were not distinguishable from one another in the ^{1}H NMR spectrum because of free and rapid rotation around the bond connecting two pyridyl units. Thus, the protons H_a's in both R and R′ appear as a single peak near δ 4.8; the H_b's appear as a single peak near δ 2.4. When palladium complex **2a** is formed, each of the single peaks splits into a doublet. Peak separation between the H_a's, as well as between the H_b's, in the two sets of heptyl groups is now

(14) ^{1}H NMR of $PdCl_2$(pyridine)$_2$ complex **8** in $(CDCl_2)_2$: δ 8.80 (H_2, 2H), 7.82 (H_4, 1H), 7.37 (H_3, 2H).^{1}H NMR of free pyridine in $(CDCl_2)_2$: δ 8.58 (H_2, 2H), 7.68 (H_4, 1H), 7.29 (H_3, 2H).

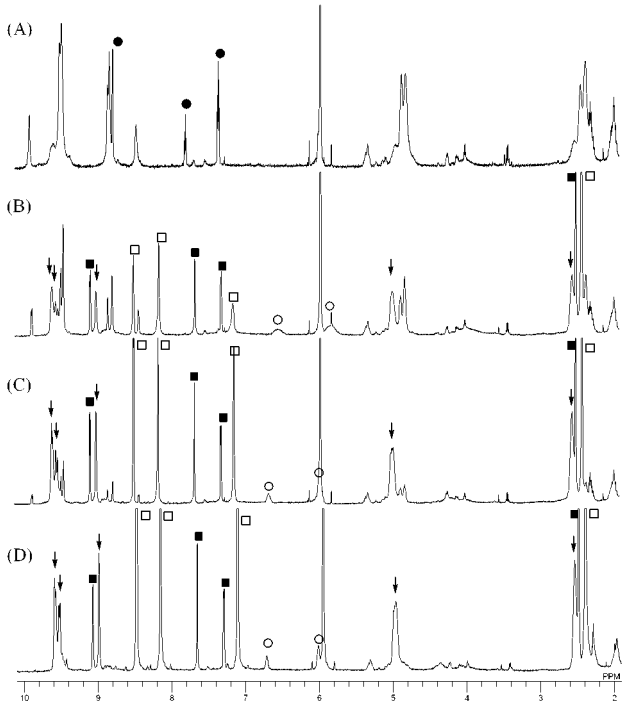


Figure 3. ^{1}H NMR titration of **2a** with 4,4′-dimethyl-2,2′-bipyridine **9** (600 MHz, $(CDCl_2)_2$). (A) **2a** (1.6 μM, the same spectrum as Figure 1D). (B) A + **9** (1.3 equiv). (C) A + **9** (2.7 equiv). (D) A + **9** (6.8 equiv) = **1a** + **10**. (○) Coordinated axial pyridine, (●) $PdCl_2$(pyridine)$_2$ **8**, (□) **9**, (■) **9**−$PdCl_2$ complex (**10**).

detectable because of differences in distances from the facing porphyrin plane. These results show that the addition of 2.2 equiv of Pd(II) completely converts the compound from a freely rotating conformation to an open-mouth one even at such an extremely dilute solution as 1.6 μM.[15]

Next, to break the cofacial conformation of bisporphyrin **2a**, 4,4′-dimethyl-2,2′-bipyridine **9** was added to the mixture. The reaction course was monitored by ^{1}H NMR spectrometry (Figure 3). When 1.3 equiv of **9** was added, signals of **8** at 8.8, 7.8, and 7.4 ppm (filled circles in Figure 3A) disappeared completely with concomitant appearance of signals of coordinating pyridines at 6.5 and 5.8 ppm (open circles in Figure 3B). Upon further addition of **9**, signals of palladium complex **2a** decreased, and uncomplexed bisporphyrin **1a** (indicated as arrows) increased. Finally, the addition of 6.8 equiv of **9** eliminated almost all of the signals of **2a**, and signals of bisporphyrin **1a** (arrows), **9**−$PdCl_2$ complex (**10**) (filled squares), and free **9** (open squares) were observed (Figure 3D). Signals of pyridine coordinated to zincporphyrin then reappeared at 6.7 and 6.1 ppm (Figure 1B). These results are summarized in Figure 4, where reversible complexation of the bipyridyl part with $PdCl_2$ controls the orientation of two porphyrins along with the axial ligation of pyridines.

Conclusion

We have established a facile synthetic method of bipyridylene-bridged bisporphyrin **1a** by a nickel-mediated homocoupling reaction. The homocoupling reaction conditions are mild and expected to be applicable to the synthesis of other bipyridyl- and biarylbisporphyrins having functional groups after further suitable optimization for each porphyrin. The addition of 2.2 equiv of palladium chloride to **1a** converted the freely rotating conformation to the cofacial bisporphyrin **2a**. The subsequent addition of 4,4′-dimethyl-2,2′-bipyridine **9** regenerated the initial conformation of bisporphyrin **1a**. In this manner, spatial geometries of two porphyrins were easily regulated by reversible complexation of the bipyridyl part. Cofacial porphyrin with a unit capable of reversible on−off complexation may be utilized as a molecular switch in supramolecular chemistry.

Experimental Section

General Methods. NMR spectra were obtained from JEOL EX-270 and ECP-600 instruments. ^{1}H NMR chemical shifts are reported in parts per million (ppm) from tetramethylsilane (0 ppm) in $CDCl_3$ and $(CDCl_2)_2$. UV−vis spectra were obtained from a Shimadzu UV-3100PC instrument. MALDI-TOF mass spectra were measured with a Perseptive Biosystems Voyager DE-STRapparatus. Dithranol purchased from SIGMA was used as a matrix in MALDI-TOF mass spectrometric measurements. Chromatographies were performed by using Merck silica gel 60 (0.063~0.200 mm). Thin layer chromatographies were performed on commercial Merck silica gel 60F254 plates. $Ni(cod)_2$ was prepared according to the literature.[16]

***meso*-(*n*-Heptyl)dipyrromethane (4a).**[17] Trifluoroacetic acid (0.152 mL, 2 mmol) was added to a solution of 1-octanal (3.2 mL, 20 mmol) and pyrrole (56 mL, 800 mmol) in deoxygenated $CHCl_3$. After stirring for 5 h at room temperature and addition of 0.1 N NaOH solution (100 mL), and the mixture was extracted with $CHCl_3$ (100 mL × 3). The organic layer was washed with water (100 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude mixture was distilled under reduced pressure to remove pyrrole and then to give dipyrromethane **4a** (4.08 g, 16.7 mmol, 83%, bp 190 °C/0.14 mmHg) as a colorless oil: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.73 (s, 2H), 6.62 (dd, 2H, J = 5.4, 2.7 Hz), 6.14 (dd, 2H, J = 5.4, 2.7 Hz), 6.05 (dd, 2H, J = 5.4, 2.7 Hz), 3.95 (t, 1H, J = 7.0 Hz), 1.92 (dt, 2H, J = 7.0, 7.0 Hz), 1.40−1.10 (m, 10H), 0.87 (t, 3H, J = 7.0 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 133.9, 117.3, 107.9, 105.8, 37.6, 34.5, 32.0, 29.6, 29.4, 27.7, 22.8, 14.3. Anal. Calcd for $C_{16}H_{24}N_2$: C, 78.64; H, 9.90; N, 11.46. Found: C, 78.61; H, 10.00; N, 11.52.

5,10,15-Tris(*n*-heptyl)-20-(2′-bromo-4′-pyridyl)porphyrin (5a). Trifluoroacetic acid (0.91 mL, 10.7 mmol) was added to a solution of 2-bromopyridine-4-aldehyde[18] (1.0 g, 5.38 mmol), 1-octanal (0.84 mL, 5.38 mmol), and dipyrromethane **4a** (2.62 g, 10.7 mmol) in deoxygenated $CHCl_3$ (1.06 L). After the mixture was stirred for 1 h at room temperature, 2,3,5,6-tetrachloro-1,4-benzoquinone (chloranil, 3.97 g, 16.7 mmol) was added to the mixture to perform oxidative aromatization. After the mixture was stirred for 1 h, 0.1 N NaOH solution was added, and the mixture was extracted with $CHCl_3$. The organic layer was washed with 0.1 N NaOH solution, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, 1/1 benzene/hexane) to give **5a** (480 mg, 12%) as a purple solid: mp 86−91 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.54 (d, 2H, J = 4.4 Hz), 9.50 (d, 2H, J = 4.4 Hz), 9.43 (d, 2H, J = 5.1 Hz), 8.74 (d, 1H, J = 5.1 Hz), 8.73 (d, 2H, J = 5.1 Hz), 8.33 (s, 1H), 8.06 (d, 1H, J = 5.1 Hz), 4.98 (t, 2H, J = 8.1 Hz), 4.92 (t, 1H, J = 8.1 Hz), 2.54 (t, 1H, J = 8.1 Hz), 2.52 (t, 1H, J = 8.1 Hz), 1.83 (t, 1H, J = 8.1 Hz), 1.80 (t, 1H, J = 8.8 Hz), 1.75−1.20 (m, 18H), 0.95−0.87 (m, 9H), −2.70 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.0

(15) In this case, 1 equiv of $PdCl_2$ was used to form **2a**, and 1 additional equiv was used to abstract coordinated pyridines. During the course of the addition of $PdCl_2$, a mixture of **2a**, $PdCl_2$(pyridine)$_2$ **8**, and **1a** was observed by ^{1}H NMR.

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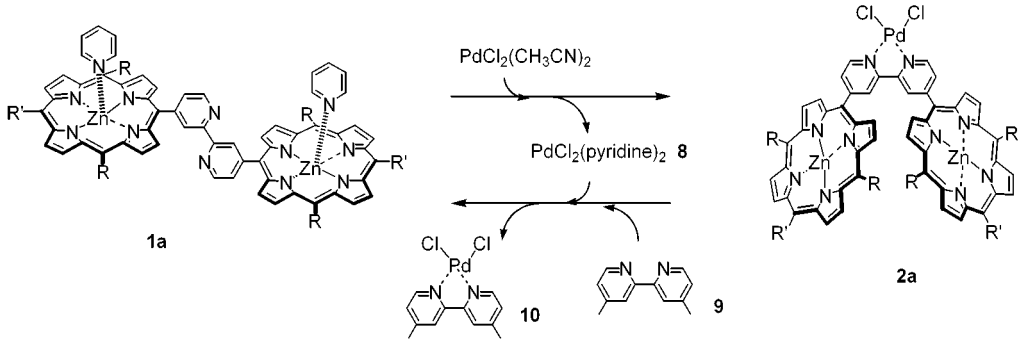

Figure 4. Reversible conversion between **1a** and **2a**.

(C), 148.1(PyCH), 141.3(C), 133.4 (PyCH), 131−128 (very broad, β carbons of porphyrin), 128.6 (PyCH), 120.9 (C), 120.0 (C), 112.3 (C), 39.1 (CH_2, b′), 38.9 (CH_2, b), 36.0 (CH_2, a′), 35.5 (CH_2, a), 32.03 (CH_2, d′), 31.99 (CH_2, d), 30.7 (CH_2, c′), 30.6 (CH_2, c), 29.5 (CH_2, e, e′), 22.8 (CH_2, f, f ′), 14.2 (CH_3, g, g′) (signals of α carbons of pyrroles were missing because of broadening); MALDI-TOF mass (dithranol) *m/z* 760.6 $(M + H)^+$, calcd for $C_{46}H_{58}BrN_5$ 759.39; UV−vis (λ_{max}/nm (abs.), $CHCl_3$) 419.5 (0.114), 520.5 (0.005), 557.0 (0.003), 593.0 (0.001), 655.0 (0.002).

5,10,15-Tris(*n*-heptyl)-20-(2′-bromo-4′-pyridyl)porphyrinatozinc (3a). Saturated zinc acetate solution in MeOH (20 mL) was added to a solution of **5a** (480 mg, 0.630 mmol) in $CHCl_3$ (50 mL) while the mixture was stirred. After stirring for 1 h at room temperature, the mixture was washed with water (100 mL × 3), dried over Na_2SO_4, and evaporated under reduced pressure to give purple solid **3a** (458 mg, 0.556 mmol, 88%): mp 136−141 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.18 (d, 1H, J = 4.4 Hz), 8.79 (d, 1H, J = 4.4 Hz), 8.74 (d, 1H, J = 4.4 Hz), 8.64 (d, 1H, J = 4.4 Hz), 8.59 (d, 1H, J = 4.4 Hz), 8.34 (s, 1H), 7.96 (d, 1H, J = 4.4 Hz), 4.40−4.32 (m, 4H), 4.14−4.06 (m, 2H), 2.35−2.26 (m, 4H), 2.18−2.09 (m, 2H), 1.79−1.71 (m, 4H), 1.71−1.64 (m, 2H), 1.40−1.20 (m, 18H), 0.98−0.085 (m, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.6 (C), 148.7 (C), 148.6 (C), 147.6 (C), 147.6 (PyCH), 147.3 (C), 140.7 (C), 133.6 (PyCH), 130.0 (βCH), 128.9 (βCH), 128.7 (PyCH), 128.0 (βCH), 127.6 (βCH), 120.3 (C), 119.8 (C), 112.5 (C), 39.0 (CH_2), 38.8 (CH_2), 35.1 (CH_2), 35.0 (CH_2), 32.2 (CH_2), 32.1 (CH_2), 30.8 (CH_2), 30.7 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 23.0 (CH_2), 14.4 (CH_3); MALDI-TOF mass (dithranol) *m/z* 822.7 $(M + H)^+$, calcd for $C_{46}H_{56}BrN_5Zn$ 821.3; UV−vis (λ_{max}/nm (abs.), $CHCl_3$) 423.5 (0.273), 556.5 (0.014), 598.5 (0.006). Anal. Calcd for $C_{46}H_{56}BrN_5Zn\cdot H_2O$: C, 65.59; H, 6.94; N, 8.31. Found: C, 66.17; H, 6.84; N, 7.60.

Bipyridylbisporphyrin (1a). Dry DMF (50 mL) and cyclooctadiene (69 μL, 0.105 mmol) were added to bromopyridylporphyrin **3a** (25 mg, 0.033 mmol) and 2,2′-bipyridine (6.5 mg, 0.042 mmol) in a Schlenk flask (100 mL) under an argon atmosphere. After the mixture was stirred for 5 min, $Ni(cod)_2$ (220 mg, 0.8 mmol) was added and the mixture was stirred for 24 h at room temperature. DMF was evaporated under reduced pressure, and the residue was dissolved into $CHCl_3$ (50 mL). The chloroform solution was washed with 5% ethylenediaminetetraacetic acid solution adjusted to pH 12 (30 mL × 5) to remove excess nickel species. The organic layer was dried over Na_2SO_4 and evaporated in vacuo. The crude mixture of bisporphyrin **1a** and monoporphyrin **7a** was separated roughly first by using Bio-Beads S-X1 (Bio-Rad Laboratories 200−400 mesh, polystyrene, exclusion limit 14 000, eluent: toluene). Further purification was performed by use of recycle HPLC (Japan Analytical Industry, LC-908) attached to a GPC column (Tosoh TSK-GEL $G2500H_{HR}$, exclusion limit 20 000) with pyridine as an eluent to give pure **1a** (15.7 mg, 58%) as a purple solid. **1a**: mp 45−60 °C; ^{1}H NMR (20 μM in $(CDCl_2)_2$, 600 MHz, 25 °C) δ 9.65−9.58 (β_3, β_4, m, 8H), 9.59−9.50 (H_3, m, 2H), 9.58−9.55 (β_2, m, 4H), 9.01−8.98 (β_1, m, 4H), 9.01−8.98 (H_6, m, 2H), 8.20−8.16 (H_5, m, 2H), 6.58 (PyH_4, br, 2H), 5.84 (PyH_3, br, 4H), 5.10−4.98 (H_a, m, 12H), 3.65 (PyH_2, br, 4H), 2.62−2.48 (H_b, m, 12H), 1.85−1.75 (H_c, m, 12H), 1.65−1.48 (H_d, m, 12H), 1.45−1.30 (H_e, H_f, m, 24H), 0.99−0.80 (H_g, m, 18H); ^{13}C NMR (20 μM in $(CDCl_2)_2$, 150 MHz, 25 °C) δ 154.68, 153.52, 150.06, 149.94, 149.30, 148.42, 147.49, 144.60 (PyC_2), 135.87 (PyC_4), 131.16, 130.08, 129.42, 129.35, 129.11, 127.47, 122.54 (PyC_3), 121.03, 120.26, 115.14, 39.45 ($C_{b'}$), 39.40 (Cb), 36.15 (Ca′), 36.02 (Ca), 32.22 (Cf, Cf ′), 30.84 (Cc, Cc′), 29.66 (Cd, Cd′), 22.99 (Ce, Ce′), 14.49 (Cg, Cg′); UV−vis (λ_{max}/nm (abs.), $CHCl_3$) 300.5 (0.014), 428.0 (0.157), 557.5 (0.094), 599.0 (0.004); MALDI-TOF mass *m/z* 1486.0 (**1a**−2pyridine + $H)^+$, calcd 1484.8 (**1a**−2pyridine = $C_{92}H_{112}N_{10}Zn_2$).

Palladium Complex (2a). A solution of $PdCl_2(CH_3CN)_2$ in acetonitrile (6.17 × 10^{-2} M, 50 μL, 3.16 μmol) was added to a solution of bisporphyrin **1a** (4.7 mg, 3. 16 μmol) in $CHCl_3$ (20 mL). After the mixture was stirred for 1 h at room temperature, the solvent was removed under reduced pressure. The residual solid was washed with methanol (10 mL × 3) and dried under reduced pressure to give purple solids **2a** (4.0 mg, 76%). **2a**: ^{1}H NMR ($(CDCl_2)_2$, 600 MHz, 25 °C) δ 9.93−9.91 (H_6, m, 2H), 9.56−9.44 (β_2, β_3, β_4, m, 12H), 8.88−8.81 (β_1, m, 4H), 8.88−8.81 (H_3, m, 2H), 8.50−8.46 (H_5, m, 2H), 4.90−4.85 ($H_{a'}$, m, 4H), 4.85−4.78 (H_a, m, 8H), 2.50−2.41 ($H_{b'}$, m, 4H), 2.41−2.35 (H_b, m, 8H), 1.65−1.15 (H_d, $H_{d'}$, H_e, $H_{e'}$, H_f, $H_{f'}$, m, 36H), 0.92−0.84 ($H_{g'}$, m, 6H), 0.86−0.75 (H_g, m, 12H); UV−vis (λ_{max}/nm (abs.), $CHCl_3$) 312.0 (0.013), 422.0 (0.092), 562.5 (0.009), 616.5 (0.002); MALDI-TOF mass *m/z* found 1661.9 $(M + H)^+$, calcd 1660.61 ($C_{92}H_{112}C_{l2}N_{10}PdZn_2$).

NMR Spectral Measurements. $PdCl_2(CH_3CN)_2$ was added portionwise to the solution of bisporphyrin **1a** (1.2 mg, 0.81 μmol) in $(CDCl_2)_2$ (0.5 mL), and the mixture was sonicated for 2 min in an NMR sample tube. An NMR spectrum was recorded after each addition to monitor the reaction course (Figure 1). After the complete formation of **2a**, 4,4′-dimethyl-2,2′-bipyridine **9** was added potionwise to the mixture, and the mixture was sonicated for 2 min. NMR spectra were similarly recorded to monitor the reaction (Figure 3).

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of **4a**, **5a**, **3a**, **1a**, and **2a** (only ^{1}H NMR). This material is available free of charge via the Internet at http://pubs.acs.org.

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