Porphyrrins

Control of Conformation and Chirality of Nonplanar π-Conjugated Diporphyrins Using Substituents and Axial Ligands

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Abstract: Nonplanar conformations of pyrazine-fused ZnII diporphyrins could be controlled by the choice of the meso-aryl substituents and an axial ligand on the central metals. ZnII diporphyrins bearing sterically demanding meso-aryl groups with ortho-substituents led to a twisted chiral D2 conformation, while an achiral C2h form was preferred in the case of aryl groups without ortho-substituents. Helical chirality induction on ZnII diporphyrins in the twisted conformation was achieved by controlling their handedness of the molecular twist through coordination of optically active 1-phenethylamine.

Introduction

Nonplanar π-conjugated molecules have been extensively studied in recent years because of their unique structure and properties.[1] In particular, distortion of a planar π-system offers intriguing characteristics such as chiroptical properties, dynamic behavior, and anisotropic charge transfer. One of the examples of such distorted π-conjugated molecules is twisted acenes.[2,3] Pascal and co-workers reported the synthesis of a highly twisted pentacene, which has an overall twisting angle of 144.8°.[2b,c] In general, twisted acenes have two conformations, twisted chiral and achiral forms.[3] Achiral forms are sometimes predominant in the solid state.[3b] If the isomerization barrier between two conformers is high enough, they can be separated.[3d] However, it is not trivial to obtain the twisted conformation selectively. Moreover, the helicity control of twisted acenes by some external stimuli has not yet been achieved to date.

Recently, we have reported the synthesis of highly twisted NiII pyrazine-fused diporphyrins with a twisted chiral D2 conformation.[4] These twisted diporphyrins show a dynamic twist inversion behavior in solution, as judged from the analysis of their NMR spectra. In contrast, Paolesse et al. have elucidated an achiral C2h conformation for a similar ZnII pyrazine-fused diporphyrin with meso-phenyl groups.[5] A similar NiII diporphyrin with meso-phenyl groups was also prepared by Bringmann et al. and us without structure elucidation by X-ray analysis.[6] We were then interested in the different D2 and C2h conformations of these diporphyrins and decided to investigate the effects of meso-substituents and central metals on the conformational preference.

The central metals and the substituents affect the conformation of the porphyrin skeleton.[7] An axial ligand also modifies the structure of the porphyrin. For example, chirality can be installed in achiral metalloporphyrins through deformation of the porphyrin structure.[8] Consequently, the conformation of porphyrins can be fine-tuned by an axial ligand, central metals, and peripheral substituents.

Herein, we report the conformational control between D2 and C2h forms of pyrazine-fused diporphyrins using meso-substituents (Figure 1). Furthermore, we demonstrate the chirality induction on the twisted conjugated diporphyrins by controlling their handedness through coordination of an optically active ligand on the central metals.

Figure 1. Several conformations of nonplanar pyrazine-fused diporphyrins.
Results and Discussion

To prepare Zn\(^{II}\) diporphyrin complexes, we initially performed demetallation of the Ni\(^{II}\) diporphyrins 1Ni (Ar = 2,4,6-trimethylphenyl) and 2Ni (Ar = 4-tert-butyl-2,6-dimethylphenyl) with H\(_2\)SO\(_4\) in trifluoroacetic acid (TFA).

Unfortunately, 1Ni and 2Ni decomposed under these strongly acidic conditions. Treatment of 1Ni and 2Ni with p-tolylmagnesium bromide in toluene afforded the corresponding free-base diporphyrins 1H and 2H in 87% and 81% yields, respectively (Scheme 1).

Subsequent metallation of these free-base diporphyrins with Zn(OAc)\(_2\) furnished Zn\(^{II}\) diporphyrins 1Zn and 2Zn. On the other hand, treatment of 3Ni (Ar = 4-tolyl) with H\(_2\)SO\(_4\) in TFA provided free-base 3H in good yield. Because of its low solubility, 3H was converted to 3Zn without further purification. These Zn\(^{II}\) diporphyrins were characterized by NMR spectroscopy and high-resolution mass spectrometry analyses.

The structures of Zn\(^{II}\) diporphyrins 1Zn, 2Zn, and 3Zn were elucidated by X-ray diffraction analysis. Both 1Zn and 2Zn adopt a twisted D\(_2\) conformation. Two methanol molecules ligate to the zinc centers from the same side of diporphyrins (Figure 2a–c and Figure S15). The edge-to-edge twisting angles of 1Zn and 2Zn are 47.1\(^\circ\) and 35.4\(^\circ\), respectively. The twist angles of the pyrazine ring in 1Zn and 2Zn are 14.1\(^\circ\) and 15.3\(^\circ\), respectively, which are greater than those in the corresponding Ni\(^{II}\) diporphyrins 1Ni (13.0\(^\circ\)) and 2Ni (13.2\(^\circ\)). In contrast, the twist angles of the porphyrin units in Zn\(^{II}\) diporphyrins 1Zn (15.4\(^\circ\) and 17.7\(^\circ\)) and 2Zn (9.9\(^\circ\) and 9.9\(^\circ\)) are significantly lower than those in Ni\(^{II}\) diporphyrins 1Ni (56.3\(^\circ\) and 56.3\(^\circ\)) and 2Ni (61.7\(^\circ\) and 61.3\(^\circ\)). The difference in the twist angles of the porphyrin units can be explained by the general trend of porphyrin deformation.[11] The Zn\(^{II}\) porphyrin ring in 1Zn and 2Zn adopt domed conformations, whereas the Ni\(^{II}\) porphyrin ring 1Ni and 2Ni exhibit ruffled structures with larger twist angles. These results clearly indicated that the central metal has an important role in changing the twisting angle of twisted diporphyrins. On the other hand, 3Zn adopts C\(_{2h}\) conformation judging from its X-ray diffraction analysis (Fig-

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**Scheme 1.** Synthesis of Zn\(^{II}\) diporphyrins 1Zn, 2Zn, and 3Zn. Reaction conditions: (i) 4-MeC\(_6\)H\(_4\)MgBr, toluene, 80 \(^\circ\)C, 20 h; then conc. HCl; (ii) H\(_2\)SO\(_4\), CF\(_3\)COOH, RT, 3 h. (iii) Zn(OAc)\(_2\)-2H\(_2\)O, toluene/MeOH, 120 \(^\circ\)C, 10–17 h.

**Figure 2.** X-ray crystal structure of 2Zn and 3Zn. a) Top view, b) front view, and c) side view of 2Zn and d) perspective view and e) front view of 3Zn. Hydrogen atoms in a) and meso-aryl groups in c) and d) are omitted for clarity. The thermal ellipsoids are scaled to a probability level of 50\%.
ure 2d, e). This result is consistent with the structure of a similar diporphyrin ZnII complex with phenyl substituents reported by Paolese et al.\(^1\) Two methanol molecules in 3Zn coordinate to zinc atoms in an antiparallel fashion in contrast to the cases of 1Zn and 2Zn. Such a different conformation among 1Zn, 2Zn, and 3Zn indicates that the molecular twisting is mainly induced by meso-aryl groups. In addition, the ortho-substituents on the aryl groups are essential to determine whether the molecule preferentially adopts D\(_2\) or C\(_{2h}\) conformation.

Figure 3 and Figure S6 show UV/Vis absorption and CD spectra of 1Zn, 2Zn, and 3Zn both in the absence and presence of chiral amines.\(^2\) Upon the addition of enantiomerically pure (R)- or (S)-1-phenylethylamine (4) to ZnII diporphyrins, bathochromic shifts in the UV/Vis absorption spectra were observed (Figure 3, bottom). The coordination of the amine also induced significant changes in the CD spectra (Figure 3, top). Firstly, no CD signal was observed for a CH\(_2\)Cl\(_2\) solution of 1Zn, 2Zn, and 3Zn. Upon the addition of (R)-4, a positive Cotton effect was observed at the Q-band region near 640 nm. On the other hand, a negative Cotton effect was detected upon addition of (S)-4 in the case of 1Zn and 2Zn. Clearly, coordination of the optically active amine on zinc atoms of 1Zn and 2Zn resulted in chiral induction of the twisted diporphyrins by affecting their twist inversion behavior.\(^3\) The association constants \(K_{assoc}\) between the ZnII diporphyrins and (R)-4 were determined from the Hill plot of the data obtained from UV/Vis absorption and CD titration experiments (Figures S8–S10). The \(K_{assoc}\) of 1Zn and 2Zn were 8.0 \times 10^2 and 7.6 \times 10^1 M\(^{-1}\), respectively (Figures S11, S12). In sharp contrast, 3Zn showed no Cotton effect even in the presence of (R)-4. This result strongly suggests that p-tolyl-substituted diporphyrin 3Zn adopted the C\(_{2h}\) conformation not only in the crystal but also in solution.

Chiral induction on the ZnII-twisted diporphyrin by an optically active ligand was also monitored by NMR spectroscopy. Upon the addition of (R)-4 to a CDCl\(_3\) solution of 2Zn, several proton signals were shifted and split into two sets of peaks (Figure 4a). These signals were assigned as two diastereomers formed by coordination of the two chiral ligands to both zinc metal centers. The diastereomeric ratio was 65:35, as judged by the integration of resolved singlet \(^1\)H signals. The structure of 2Zn coordinated with (R)-4 was elucidated by X-ray diffraction analysis (Figure S16). However, the two diastereomers existed in a 1:1 ratio in the crystal, probably because the energy difference between two diastereomers is rather small.

To gain information on the twist inversion behavior, the chiral amine on zinc was removed from complexes 1Zn and 2Zn by the addition of an acid. We found that acetic acid was suitable to remove the amine without demetallation. After the addition of acetic acid, the CD intensity of 2Zn slowly decreased upon the addition of acetic acid (Figure 5a, gray line). On the other hand, the CD intensity of 2Zn instantly disappeared, indicating racemization of the helical chirality due to rapid twist inversion (Figure 5a, black line). On the other hand, the CD intensity of 2Zn slowly decreased upon the addition of acetic acid (Figure 5a, gray line). On the basis of the observed decay profile of the CD intensity, the rate constant of twist inversion of 2Zn was determined to be 5.15 \times 10^{-3} s\(^{-1}\) at 263 K assuming first-order kinetics (Figure 5). In addition, the kinetic analysis at different temperatures revealed that the activation energy for twist inversion of 2Zn is 62.2 kJ mol\(^{-1}\) (Figure S13).

Space-filling models of the two diastereomeric complexes (P,P)-2Zn-(R)-4 and (M,M)-2Zn-(R)-4 in the crystal are shown in Figure 6. The phenyl group of (R)-4 interferes at two points

![Figure 3](image-url)  
**Figure 3.** Circular dichroism (CD) (top) and UV/Vis absorption (bottom) spectra of 2Zn and 3Zn with (R)- or (S)-1-phenylethylamine 4 in CH\(_2\)Cl\(_2\).

![Figure 4](image-url)  
**Figure 4.** The aromatic region of \(^1\)H NMR spectra of 2Zn (5.8 \times 10^{-4} M) in CDCl\(_3\) at 298 K a) in the presence of (R)-4 (5.8 \times 10^{-2} M) and b) in the absence of the ligand.
with the meso-aryl groups of diporphyrin \((P,P)\)\textsubscript{2}Zn (Figure 6a), while \((R)\)\textsubscript{4} is likely to fit more easily with the cavity around the zinc center of \((M,M)\)\textsubscript{2}Zn. To confirm the relative stability of these diastereomeric complexes, we performed DFT calculations at the B3LYP/6-31G\textsuperscript{+}SDD level, which predicted that \((M,M)\)\textsubscript{2}Zn·\((R)\)\textsubscript{4} is more stable than \((P,P)\)\textsubscript{2}Zn·\((R)\)\textsubscript{4} by 13.5 kJ mol\textsuperscript{-1}. Furthermore, the circular dichroism spectra of the diporphyrins were simulated by time-dependent DFT calculations. The positive Cotton effect of \((R)\)\textsubscript{4} in the Q-band is well matched with the calculated rotatory strengths of \((M,M)\)\textsubscript{2}Zn·\((R)\)\textsubscript{4} (Figure S7). These results suggest that complexation of \((R)\)\textsubscript{4} to \(2\text{Zn}\) induces predominantly more stable \((M,M)\)-chirality in the molecular twist.

**Conclusions**

In summary, we have achieved the synthesis of Zn\textsuperscript{II} diporphyrins fused with a pyrazine unit. The conformation of these non-planar diporphyrins could be controlled to either twisted chiral \(D_2\) or achiral \(C_{2v}\) forms by the choice of meso-aryl substituents and central metals. The twisted \(D_2\) conformation is dominant both in the solid and solution states in diporphyrins with ortho-substituted sterically demanding aryl groups, while diporphyrins with ortho-unsubstituted aryl groups prefer \(C_{2v}\) forms. Helical chirality could be induced on the twisted diporphyrins by controlling their handedness through coordination of a chiral amine.

**Experimental Section**

**Instrumentation and Materials:** \(^1\)H NMR (500 MHz) and \(^{13}\)C NMR (126 MHz) spectra were recorded on a Bruker AVANCE III HD spectrometer, and chemical shifts were reported as the delta scale in ppm relative to CHCl\textsubscript{3} (\(\delta = 7.260\) ppm) and CH\textsubscript{2}Cl\textsubscript{2} (\(\delta = 5.300\) ppm) for \(^1\)H NMR, and CDCl\textsubscript{3} (\(\delta = 77.0\) ppm) for \(^{13}\)C NMR. UV/Vis absorption spectra were measured in a 1 cm quartz cell on a Shimadzu UV-2550 or JASCO V670 spectrometer. Emission spectra were measured in a 1 cm quartz cell on a JASCO FP-6500 spectrometer, and absolute fluorescence quantum yields were measured by the photon-counting method using an integration sphere. The CD spectra were measured in a 1 cm quartz cell on a JASCO J-820 spectropolarimeter. Mass spectra were recorded on a Bruker micro-TOF mass spectrometer using the positive mode ESI-TOF or APCI-TOF method for acetonitrile solutions. X-ray diffraction data were taken on a Rigaku CCD diffractometer (Saturn 724 with MicroMax-007) with Varimax Mo optics using graphite monochromated Mo\textsubscript{K\alpha} radiation (\(\lambda = 0.71075\) Å) for \(1\text{Zn}, 2\text{Zn}, 3\text{Zn},\) and \(2\text{Zn}•(R)\)\textsubscript{4} and on a Bruker D8 QUEST X-ray diffractometer with a large area (10 cm 10 cm) CMOS detector (PHOTON 100) for \(3\text{Ni}\). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.
Synthesis of 1H₂: A two-necked flask containing nickel diporphyrin in 1N HCl (170.8 mg, 0.100 mmol) was evacuated and then refilled with N₂. To the flask, 20 mL of dry and degassed toluene was added. To the solution, 4-methylphenyl(magnesium bromide)(10.0 mL, 1.0 mol, 1.36 mL THF solution) was added. The mixture was stirred at 80°C for 20 h. The reaction was quenched with 1 mL HCl aq. (10 mL) and extracted with CH₂Cl₂ three times. The combined organic layer was washed with brine and then dried over Na₂SO₄ and concentrated in vacuo. The residue was dissolved in CH₂Cl₂. To the solution, conc. HCl was added, and the resulting mixture was stirred at rt for 12 h. The reaction was quenched with aqueous NaHCO₃ and the mixture was extracted with CH₂Cl₂. The organic layer was dried over Na₂SO₄ and evaporated. The residue was purified by silica-gel column chromatography with CHCl₃/hexane (2:3, v/v) as an eluent. Recrystallization from CHCl₃/MeOH afforded the desired compound 1H₂ as a black solid in 87% yield (138.8 mg, 0.087 mmol). 1H NMR (500 MHz, CDCl₃): δ = 8.52 (d, J = 4.5 Hz, 4H, β-H), 8.42 (s, 4H, β-H), 8.17 (d, J = 5.0 Hz, 4H, β-H), 7.26 (s, 8H, Ar-H), 6.98 (s, 8H, Ar-H), 2.58 (s, 12H, Me), 2.44 (s, 12H, Me), 1.86 (s, 24H, Me), 1.53 (s, 24H, Me), and −1.98 ppm (s, 4H, inner NH); 13C NMR (126 MHz, CDCl₃): δ = 154.6, 150.0, 145.0, 139.3, 139.0, 138.9, 137.9, 137.7, 133.6, 131.3, 128.0, 127.7, 127.2, 121.9, 114.0, 21.6, 21.53, and 21.46 ppm; UV/Vis (CH₂Cl₂): λ_max (ε) = 396 (95000), 478 (220000), 542 (420000), 541 (56000), 581 (13000), 611 nm (28000 M⁻¹ cm⁻¹); Emission (CH₂Cl₂): λ_max = 617, 669, 739 nm; HRMS (APCI-MS): m/z calcd for [C₆H₄N₄H₄]⁺ = 1589.8518 [M⁺H⁺]⁻, found: 1589.8489.

Synthesis of 1Zn: A solution of free-base diporphyrin 1H₂ (10.7 mg, 6.7 μmol) in toluene (10 mL) was refluxed with Zn(OAc)₂·2H₂O (103.5 mg, 0.47 mmol) in methanol (5 mL) for 17 h. The solvent was removed under reduced pressure, and the residue was purified by silica-gel column chromatography with CHCl₃/hexane (2:3, v/v) as an eluent. Recrystallization from CHCl₃/MeOH afforded the desired compound 1Zn as a black solid in 82% yield (129 mg, 6.28 μmol). 1H NMR (500 MHz, CDCl₃): δ = 8.57 (s, 4H, β-H), 8.52 (d, J = 4.5 Hz, 4H, β-H), 7.93 (d, J = 4.5 Hz, 4H, β-H), 7.53 (s, 4H, Ar-H), 7.45 (s, 4H, Ar-H), 7.34 (s, 4H, Ar-H), 6.83 (s, 4H, Ar-H), 2.12 (s, 12H, Me), 2.00 (s, 12H, Me), 1.66 (s, 12H, Me), 1.56 (s, 36H, tBu), 1.39 (s, 36H, tBu), and 1.14 ppm (s, 12H, Me); 13C NMR (126 MHz, CDCl₃): δ = 152.4, 150.6, 149.4, 141.9, 148.4, 147.4, 140.6, 139.4, 138.9, 138.6, 138.4, 132.1, 130.3, 129.0, 127.9, 124.4, 114.6, 21.8, and 21.7 ppm; UV/Vis (MeOH): λ_max (ε) = 407 (13000), 495 (220000), 596 (80000), 634 nm (17000 M⁻¹ cm⁻¹); Emission (CH₂Cl₂): λ_max = 639, 703 nm; HRMS (APCI-MS): m/z calcd for [C₆H₄N₄ZnH₄]⁺ = 2054.0576 [M⁺H⁺]⁺, found: 2054.0560. Single crystals for 1Zn and 2Zn·(R)-4 were obtained by vapor diffusion of methanol into a chlorobenzene solution.

Synthesis of 3Ni: A Schlenk tube containing 2-amino-5,10,15,20-tetrakis(4-methylphenyl)porphyrin Ni₄[N₄] (563 mg, 7.58 μmol) was evacuated and then refilled with N₂. To the tube, 5 mL of dry and degassed CH₂Cl₂ was added. To the solution, a solution of DDQ (38.1 mg, 0.168 mmol) in dry and degassed CH₂Cl₂ (20 mL) was added and the mixture was stirred at room temperature for 14 h. The reaction was quenched with aqueous Na₂SO₄, and the mixture was extracted with CHCl₃. The organic layer was dried over Na₂SO₄ and concentrated in vacuo. The mixture was purified by silica-gel column chromatography with CHCl₃/hexane (1/3, v/v) as an eluent. The second fraction as brown band was collected and evaporated to give the desired compound 3Ni (21%, 11.53 mg, 7.80 μmol) as a brown solid. 1H NMR (500 MHz, CDCl₃): δ = 8.60 (s, 4H, β-H), 8.54 (d, J = 5.0 Hz, 4H, β-H), 8.05 (d, J = 4.5 Hz, 4H, β-H), 7.83 (d, J = 6.5 Hz, 8H, Ar-H), 7.45 (d, J = 8.0 Hz, 8H, Ar-H), 7.30 (d, J = 8.0 Hz, Ar-H), 7.00 (d, J = 8.0 Hz, 8H, Ar-H), 2.61 (s, 12H, Me), and 2.43 ppm (s, 12H, Me); 13C NMR (126 MHz, CDCl₃): δ = 147.3, 144.7, 141.7, 140.4, 137.6, 137.1, 136.5, 133.8, 133.3, 132.8, 132.6, 132.3, 131.6, 127.8, 127.4, 120.5, 115.8, 21.6, and 21.4 ppm; UV/Vis (CH₂Cl₂): λ_max (ε) = 417 (120000), 458 (110000), 488 (160000), 583 (53000), 620 nm (19000 M⁻¹ cm⁻¹); HRMS (APCI-MS): m/z calcd for [C₆H₄N₄Ni₄H₄]⁺ = 1477.4372 [M⁺H⁺]⁺, found: 1477.4303. Single crystals for X-ray diffraction analysis were obtained by vapor diffusion of methanol into its chlorobenzene solution.

Synthesis of 3Zn: To a solution of Ni²⁺ diporphyrin 3Ni (8.99 mg, 6.1 μmol) in trifluoroacetic acid (3 mL) was added an excess amount of H₂SO₄ aq. (98%, ca. 1 mL). The mixture was stirred at room temperature for 3 h. The resulting mixture was neutralized with saturated NaHCO₃ aq. and extracted with CHCl₃. The organic layer was room temperature for dry on Na₂SO₄ and evaporated. The resulting mixture
Crystallographic data for 1Zn (CCDC 1443473) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre: C_{28}H_{35}ClN_{4}O_{2}Zn, M_{w} = 2301.13, triclinic, P1, a = 15.653(8), b = 18.866(9), c = 23.070(12) Å, α = 97.930(3), β = 108.4206(5), γ = 107.4857(7), V = 59575(3) Å³, Z = 2, R = 0.0976 (I > 2σ(I)), R_{w} = 0.0305 (all data), GOF = 1.064.

Crystallographic data for 2Zn (CCDC 1443474) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre: C_{30}H_{38}ClN_{4}O_{2}Zn, M_{w} = 2245.76, orthorhombic, Pbcn, a = 33.217(4), b = 12.5407(11), c = 31.343(4) Å, V = 13056(3) Å³, Z = 4, R = 0.0607 (I > 2σ(I)), R_{w} = 0.1819 (all data), GOF = 1.071.

Crystallographic data for 3Zn (CCDC 1443476) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre: C_{30}H_{38}ClN_{4}O_{2}Zn, M_{w} = 1727.73, monoclinic, P2_{1}/n, a = 17.004(16), b = 17.432(17), c = 31.063(6) Å, β = 92.150(15), V = 9200(16) Å³, Z = 4, R = 0.1798 (I > 2σ(I)), R_{w} = 0.0502 (all data), GOF = 1.200.

Crystallographic data for 2Zn(r):4Zn (CCDC 1443475) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre: C_{30}H_{38}ClN_{4}O_{2}Zn, M_{w} = 2295.73, orthorhombic, P2_{1}2_{1}2_{1}, a = 31.077(8), b = 34.026(9), c = 12.598(3) Å, V = 13321(6) Å³, Z = 4, R = 0.0801 (I > 2σ(I)), R_{w} = 0.2296 (all data), GOF = 1.057.

Crystalllographic data for 3Ni (CCDC 1443477 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre: C_{30}H_{38}ClN_{4}O_{2}Ni, M_{w} = 1704.12, orthorhombic, Fdd2, a = 28.5294(17), b = 32.8373(2), c = 17.2302(10) Å, V = 16141.51(17) Å³, Z = 8, R = 0.0729 (I > 2σ(I)), R_{w} = 0.1911 (all data), GOF = 1.104.

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