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Synthesis and characterizations of free base and Cu(II) complex of a porphyrin sheet

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ABSTRACT

Free base porphyrin sheet **5** was prepared by demetalation of zinc complex **1**, which was now more conveniently prepared in 30% yield by oxidation of a mixture of tetraporphyrins, **8**, **9**, and **11**. The ¹H NMR spectrum of **5** shows no indication of an aromatic ring current for the porphyrin rings and evidences the freezing of the pyrrolic NH protons at the most inner and outer corner positions, both of which contrast sharply with strong aromatic ring currents and rapid NH tautomerism of normal porphyrins. DFT calculations supported the experimental results, suggesting that the enforced planar COT core causes these unique properties. The free base **5** was transformed into Cu(II) complex **6** that exhibits antiferromagnetic interaction among the Cu(II) ions with J=-1.16 cm⁻¹.

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1. Introduction

In recent years, considerable attention has been focused on the development of extensively π -conjugated porphyrins in light of their potential applications in optoelectronic devices, sensors, photovoltaic devices, photodynamic therapy pigments, and so on.¹ Most of such conjugated porphyrins have been created through introduction of π -conjugated segments at the porphyrinic peripheries.¹ Among these, *meso-meso*, $\beta-\beta$, $\beta-\beta$ triply linked (fused) porphyrin oligomers have been attracting considerable attention due to their remarkably extended π -conjugation over the flat molecular structure and characteristic electronic properties.^{2,3} As an extension of these studies, we explored the synthesis of directly fused square-planar porphyrin sheet 1 that shows anomalous induced magnetic effects.⁴ Curiously, the ¹H NMR signals of the 1,4-phenylene protons of 1,4-bis(1-methylimidazol-2-ylethynyl)benzene (2) in the 1:2 complex, $1-(2)_2$, were downfield shifted by 3.78 ppm despite their location just above the porphyrin plane (Scheme 1). This unusual complexation-induced-shift (CIS) that is opposite to the normal porphyrins has been interpreted in terms of a local paratropic ring current effect around the cyclooctatetraene (COT) core. Importantly, the COT core is forced to be planar owing to the multiply fused porphyrins in 1, plausibly causing a local antiaromatic character.² In another interesting case, **1** was dimerized with the aid of four molecules of linear bidentate ligands such as 4,4'-bipyridyl (3) to form face-to-face complex $(1)_2$ -(3)₄, in which

the pyridyl protons of **3** are also downfield shifted, serving as a nice experimental guide for height information of the induced magnetic effects of **1**.⁵

Magnetic exchange coupling between distant metal centers is a major topic in the field of magnetochemistry.⁶ Characteristic molecular and electronic structures of fused porphyrins stimulated the study on their magnetic properties, namely a long-range magnetic coupling between metal centers in porphyrin rings. Along this line, the paramagnetic Cu(II) complex of fused dimer **4** was studied, which revealed antiferromagnetic interaction between two Cu(II) ions with -J=1.43 cm⁻¹ (Fig. 1).⁷ The magnetic exchange coupling of Cu(II) complex of the porphyrin sheet is of particular interest in respect of the symmetric square tetrameric structure.

In this paper, we report the synthesis and characterization of free base porphyrin sheet **5** and its Cu(II) complex **6** (Fig. 2). The ¹H NMR spectrum of **5** shows no indication of an aromatic ring current for the porphyrin rings. The magnetic susceptibility and ESR measurements of **6** revealed the antiferromagnetic interactions among the Cu(II) ions.

2. Synthetic strategy

The previous synthesis of **1** was time-consuming and tedious, because the optical resolution of porphyrin dimers D_1 and D_2 that were prepared from 5,10-diarylporphyrin **7** was required and one isomer D_1 was used for coupling to provide porphyrin tetramers **8** and **9** and, in addition, only one isomer **9** that has free *meso*-positions at the same side was employed to furnish directly *meso-meso* linked porphyrin tetramer **10** (Scheme 2)⁸.



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Scheme 1. Molecular structure of 1 and its molecular assemblies $1-(2)_2$ and $(1)_2-(3)_4$. Ar=3,5-di-*tert*-butylphenyl.



Figure 1. Molecular structure of **4**. Ar^1 =3,5-di-*tert*-butylphenyl. Ar^2 =4-*tert*-butylphenyl.

Hence the direct oxidation reaction of the racemic mixture of **8**, **9** and diastereomer **11** was examined for the synthesis of **1** (Scheme 3), in which a racemic mixture of **D**₁ and **D**₂ was used without the optical resolution for Ag(I)-promoted coupling reaction to afford a complicated mixture of porphyrin tetramers including **8**, **9**, and **11** as well as their enantiomers, and this mixture was directly used without separation for the oxidation with DDQ-Sc(OTf)₃. In this synthetic route, intermolecular coupling products and structural isomers of fused tetramer could be produced as byproducts. In order to suppress such intermolecular coupling reactions, the oxidation was carried out under dilute conditions (0.1 mM). Although repeated separations were necessary to remove byproducts, the porphyrin sheet **1** was isolated in a pure state in 30% yield. Therefore, the direct synthesis of **1** from a mixture of acyclic porphyrin tetramers is more facile and effective as compared with the previous synthesis. Demetalation of **1** was effected with TFA and H_2SO_4 in CHCl₃ solution to free base porphyrin sheet **5** in 69% yield. Matrix-assisted-laser-desorption-ionization time-of-flight (MALDI-TOF) mass spectrum showed the parent ion peak at m/z=2724.1 (calcd for [C₁₉₂H₁₉₂N₁₆]⁺=2723.7).

3. ¹H NMR spectroscopy

The ¹H NMR spectrum of **5** in CDCl₃ was guite simple and showed a D_{4h} symmetric signal pattern consisting of two signals at 7.42 (para) and 7.22 (ortho) ppm for the meso-aryl substituents, one singlet at 6.64 ppm and one doublet at 6.09 ppm for the pyrrole β protons, and two singlets at 13.32 and 12.23 ppm for the pyrrole NH protons (Fig. 3). Two signals observed for the NH protons provide strong support for the structure of 5 where the pyrroles A and C are amino-type, and the pyrroles B and D are imino-type (Fig. 2). Importantly, the structure of the other symmetric tautomer 5A was excluded because all the pyrrolic NH protons should be equivalent in this structure. The assignment of the signals of pyrrolic NH protons was confirmed by the disappearance of these peaks by the addition of D_2O . In addition, the doublet signal due to the β proton at 6.09 ppm changed to singlet upon irradiation of the NH signal at 13.32 ppm, and the coupling constant of J=2.3 Hz is typical for pyrrolic NH-β coupling.⁹ Therefore, the singlet peak at 13.22 ppm has been assigned for the NH proton of the pyrrole C. Other less



Figure 2. Molecular structures of 5 and 6. Ar=3,5-di-tert-butylphenyl.



Scheme 2. Previous synthetic scheme of **1**. Ar=3,5-di-*tert*-butylphenyl.

10

9



Scheme 3. Improved synthesis of 1. Ar=3,5-di-tert-butylphenyl.



Figure 3. ¹H NMR spectrum of 5 in CDCl₃ at room temperature.

symmetric tautomers can be eliminated because of the observed high symmetry of the ¹H NMR spectrum.

One of the most characteristic features of ¹H NMR spectrum of **5** is that the NH signals are observed in the considerably deshielded region. Usually, the inner NH protons of porphyrins are strongly shielded due to the ring currents, reflecting the aromaticity of porphyrins (Fig. 4).^{10,11} The NH proton peak of tetraphenylporphyrin **12** is observed at -2.76 ppm, while *meso*-dimethyl phlorin **13** shows its NH proton signal at 12.58 ppm.¹² The π -conjugation circuit in **13** is interrupted at the *meso*-positions, and thus there is no macrocyclic ring current. Curiously, triply linked diporphyrin **14** exhibited its NH peak at 1.42 ppm,

4. Theoretical studies

To understand the structural and electronic characteristics of free base porphyrin sheet, DFT calculations for 5 and 5A were carried out. For the calculations, model compounds $\mathbf{5}_{\mathbf{M}}$ and $\mathbf{5}\mathbf{A}_{\mathbf{M}}$ were used where 5_M and $5A_M$ represent simpler reference compounds lacking meso-aryl substituents. The structures of 5_M and 5A_M were optimized using LANL2DZ for the zinc atom and 6-31G* basis sets for the others with B3LYP method. The calculated zero point corrected energy of **5**_M is 7.4 kJ/mol lower than that of **5A**_M, which is consistent with the experimental observations. Figure 5 shows the bond lengths of the optimized structures. Both the structural optimizations of 5_{M} and $5A_{M}$ resulted in the nearly D_{4h} symmetric structures even without any symmetry restrictions. For easier illustration, the bonds shorter than 1.36 Å are indicated as double bonds, and those longer than 1.45 Å are indicated as single bonds. The intermediate bonds (1.36–1.45 Å) are represented using partial π bonds. The bond alternations (ΔR) of the COT core were 0.039 Å and 0.088 Å for $\mathbf{5}_{M}$ and $\mathbf{5}_{M}$, respectively, highlighting the significant bond alternation for the latter structure.¹³ The C^6-C^7 bond lengths in **5**_M and **5**A_M are 1.401 Å and 1.446 Å, respectively, which seemingly indicate that the COT core in $5A_M$ is more electronically isolated from the peripheral conjugated π -electron system. It is known that for planar COT, bond alternated D_{4h} conformation is more stable than π -electron delocalized D_{8h} conformation.¹⁴ Hence, the calculated results of larger bond alternation and longer C^6-C^7 bond length in the COT core in $5A_M$ seem to be compatible. On the other hand, the π -electron delocalization of the COT core with the peripheral conjugated system is more effective in 5_{M} , which con-



Figure 4. Molecular structures and ¹H NMR chemical shifts of NH of 12, 13, and 14. Ar=3,5-di-tert-butylphenyl.



Figure 5. Bond lengths of the optimized structures of 5_M (middle) and 5A_M (right). Bond lengths are written in Angstrom unit.

probably due to the weakened aromatic ring current.^{2b} The down-field shifted NH signals of **5** indicate that the aromatic ring current of porphyrin is considerably weakened or disappears. The observed different chemical shifts for the pyrrolic protons indicate the freezing of the NH tautomerism and different magnetic environments for the NH protons, where one NH proton is close to the COT core and the other is distant. Finally, during the ¹H NMR studies, we noted the chemical instability of **5** in solution, in that it changed to unidentified materials during long-period standing.

tributes the weakening of the anti-aromatic planar COT character and hence the stabilization of $\mathbf{5}_{M}$.

Nucleus-independent-chemical shift (NICS) values of 5_M and $5A_M$ were calculated by using GIAO method on the basis of the optimized structures described above.¹⁵ The center of the porphyrin ring was defined as geometric center of the internal cross.¹⁶ Figure 6 shows the calculated NICS values and the chemical shifts of the pyrrolic NH protons for 5_M and $5A_M$. The NICS values at the COT center have been calculated to be 21.7 for 5_M and 35.1 for $5A_M$, which clearly suggest the strong anti-aromatic characters at the



Figure 6. Calculated NICS values and chemical shifts (underlined) of 5_M (middle) and $5A_M$ (right).

COT core. The anti-aromatic character of the COT core in **1** has been experimentally confirmed. The NICS values at the porphyrin center have been calculated to be 1.7 for **5**_M and -6.9 for **5A**_M. The NICS value of the pyrrole ring C is more negative (-9.8) than that of the pyrrole ring A (-4.8), and calculated chemical shift of NH of pyrrole rings A and C are 10.3 and 12.3 ppm in **5**_M, respectively, but much higher chemical shift was calculated for the pyrrolic NH protons in **5A**_M. These calculations are qualitatively consistent with the ¹H NMR result. Based on the calculation results, the frozen tautomerism of **5** can be interpreted in terms of a situation that the COT core avoids an isolated 8π -electronic system through conjugation with the peripheral π -systems.

5. UV-vis-NIR absorption spectroscopy

Figure 7 shows the absorption spectra of **1** and **5** in CHCl₃. These spectra exhibit the same features containing band I around 500 nm, band II around 650–800 nm, and band III in the wavelength region longer than 1000 nm. In the previous report, the weak band III of **1** has been explained in terms of symmetry forbidden transitions due to the correct square molecular shape, in a similar manner to Gouterman's four orbital theory applied to simple porphyrin.^{2,17} The spectrum of **5** can be interpreted essentially in the same manner as that of **1**.



Figure 7. UV-vis-NIR absorption spectra of 1, 5, and 6 in CHCl₃.

6. Cu(II) complex 6

Finally, Cu(II) complex **6** was synthesized by treatment of **5** with Cu(OAc)₂ in CHCl₃ in 79% yield. The complex **6** exhibited the parent ion peak at m/z=2968.5 (calcd for [C₁₉₂H₁₈₄N₁₆Cu₄]⁺=2969.8) in MALDI-TOF mass spectrum, and exhibited an absorption spectrum

that is similar to those of 1 and 5 (Fig. 7). Figure 8 shows the result of variable-temperature magnetic susceptibility measurement of **6**. The χT value of **6** is about 1.6 emu K mol⁻¹ at 300 K, indicating the presence of four Cu(II) spins (g=2.109). The χT value is nearly constant in the temperature range of 80-300 K, and drops steeply at temperature below 20 K. then reaches to a value of $0.68 \text{ emu K mol}^{-1}$ at 2.0 K. This temperature dependence is indicative of antiferromagnetic coupling between neighboring Cu(II) ions. The inset of Figure 8 shows the schematic view of the spin Hamiltonian predicted from the molecular structure and expressed as follows, $H = I_{12} \mathbf{S_1} \cdot \mathbf{S_2} + I_{23} \mathbf{S_2} \cdot \mathbf{S_3} + I_{34} \mathbf{S_3} \cdot \mathbf{S_4} + I_{41} \mathbf{S_4} \cdot \mathbf{S_1}$, where I_{ii} denote the exchange coupling parameter between the spin site *i* and *j*. It is assumed that the four kinds of exchange coupling parameter are equivalent due to the D_{4h} symmetric molecular structure. The experimental data have been fitted with above model as shown in Figure 8. The observed values are reproduced by following parameters $J_{12}=J_{23}=J_{34}=J_{41}=-1.16 \text{ cm}^{-1}$ and g=2.109. It is revealed that the magnetic coupling is antiferromagnetic between the neighboring Cu(II) spins.

The observed powder ESR spectrum is interpreted by the random-orientation spectrum pattern including the *g*-anisotropy (Fig. 9). No fine-structure splitting attributing the coupled state with S=2 was observed due to the broad linewidth and the long Cu(II)-Cu(II) distance.⁷ From the spectral simulation, the principal values of the *g*-tensor are determined as follows, $g_1=2.075$, $g_2=2.075$, and $g_3=2.178$. In the theoretical calculation of the magnetic susceptibility, $g_{mean} (=(g_1+g_2+g_3)/3)=2.109$ was applied.



Figure 8. Variable-temperature magnetic susceptibility measurement of 6 in the range of 2–300 K. Inset indicates the schematic view of spin Hamiltonian.

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Figure 9. Observed (top) and simulated (bottom) powder ESR spectrum of 6 at 4 K.

7. Conclusions

Free base porphyrin sheet **5** was obtained by the demetalation of zinc complex **1**, which was now prepared more conveniently by the oxidation of a mixture of porphyrin tetramers **8**, **9**, and **11**. The ¹H NMR spectrum of **5** revealed that the porphyrin rings has no aromatic ring current and that the NH tautomerism is completely frozen. The DFT calculations supported the experimental results, and gave an insight that the enforced planar COT core is important for understanding of the structure of **5**. Metalation of **5** with Cu(OAc)₂ gave the Cu(II) complex **6** that exhibits the weak antiferromagnetic interactions among the Cu(II) ions as revealed by the ESR and magnetic susceptibility measurements.

8. Experimental section

8.1. General

All reagents and solvents were of commercial reagent grade and were used without further purification except where noted. Dry toluene was obtained by distilling over CaH₂. ¹H NMR spectra were recorded on a JEOL ECA-delta-600 spectrometer (600 MHz), and chemical shifts were reported as the delta scale in parts per million relative to CHCl₃ (δ =7.26 ppm). Mass spectra were recorded on a Shimadzu/KRATOS KOMPACT MALDI 4 spectrometer, using the positive-MALDI ionization method with 9-nitroanthracene or dithranol matrix. The spectroscopic grade CHCl₃ was used as solvents for all spectroscopic studies. UV-vis-NIR absorption was recorded on a Shimadzu UV-3100 spectrometer. ESR spectra were recorded on a Bruker E500 spectrometer operating at X band and equipped with an Oxford helium cryostat. To determine g values, the observed ESR spectrum was simulated by Bruker WIN-EPR Sim Fonia program. The solid-state magnetic susceptibility was measured between 2 and 300 K under a magnetic field of 0.5 T with a SQUID magnetometer (Quantum Design MPMS-5 and Quantum Design MPMS-1). The calculated magnetic susceptibility is introduced by the direct diagonalization of the spin Hamiltonian. The spin Hamiltonian parameters are determined by the computer program including the least square fitting routine written in Matlab.

8.2. Synthesis of porphyrin sheet 1 from a mixture of 8, 9, and 11

To a solution of a mixture of tetramers **8**, **9**, and **11**⁸ (1 equiv, 120 mg, 0.040 mmol) in dry toluene (400 ml) were added DDQ

(30 equiv, 273 mg, 1.2 mmol) and Sc(OTf)₃ (30 equiv, 590 mg, 1.2 mmol), and the resulting mixture was stirred for 6 h at 100 °C with shielding from light under Ar atmosphere. The reaction mixture was cooled to room temperature and diluted with THF, and then passed through an alumina column with THF. After evaporation of the solvent, the residue was dissolved in THF, poured on an alumina column, and washed with THF until the eluent became colorless. A purple fraction that still remained on the alumina column was thoroughly eluted with toluene and butylamine alternatively. This procedure was repeated more than six times. The combined THF eluent was allowed to stand about 1 day to complete precipitation, and the resulting black precipitate was filtered. The precipitate was dissolved to the combined toluene and butylamine eluent, and the solvent was evaporated. Recrystallization from CH₂Cl₂/CH₃CN afforded **1** as a black solid (as a *n*-butylamine adduct) (36.2 mg, 0.012 mmol, 30%).

8.3. Free base porphyrin sheet 5

To a solution of **1** (19.4 mg, 5.93 µmol, butylamine adduct) in 20 ml of CHCl₃ previously bubbled with N₂ for 15 min, 3 ml of TFA and five drops of concd H₂SO₄ was added at 0 °C, and resulting solution was stirred for 40 min at room temperature with shielding from light under N₂ atmosphere. The reaction mixture was added to water and extracted with CHCl₃. The organic layer was washed with NaHCO₃ (aq) and water, and dried over anhydrous Na₂SO₄, and then evaporated to remove the solvent. The residue was recrystallized from CH₂Cl₂/CH₃CN afforded **5** as a black solid (11.2 mg, 4.1 µmol, 69%). ¹H NMR (CDCl₃) δ 13.32 (s, 4H, NH), 12.23 (s, 4H, NH), 7.43 (s, 8H, Ar-*p*), 7.22 (d, *J*=1.6 Hz, Ar-*o*), 6.64 (s, 8H, Por- β), 6.09 (d, *J*=2.3 Hz, 8H, Por- β), 1.31 (s, 144H, *t*-Bu) ppm; MALDI-TOF MS *m*/*z*=2724.1, calcd for C₁₉₂H₁₉₂N₁₆ 2723.7; UV-vis (CHCl₃) $\lambda_{max}(\varepsilon)$ =508 (163,000) and 665 (89,000) nm. UV-vis (CHCl₃ with 5% v/v TFA) $\lambda_{max}(\varepsilon)$ =527 (184,000), 769 (151,000), and 1106 (23,000) nm.

8.4. Cu(II) complex 6

To a solution of **5** (11.2 mg, 4.1 µmol) in CHCl₃ (20 ml) was added a saturated solution of Cu(OAc)₂ in methanol (1 ml), and the resulting solution was stirred for 9 h at reflux with shielding from light under N₂ atmosphere. The reaction mixture was added to water and extracted with CHCl₃. The organic layer was washed with NaHCO₃ (aq) and water, and dried over anhydrous Na₂SO₄, and then evaporated to remove the solvent. The residue was recrystallized from CH₂Cl₂/CH₃CN to afford black solids of **6** (9.59 mg, 3.2 µmol, 79%). MALDI-TOF MS m/z=2968.5, calcd for C₁₉₂H₁₈₄N₁₆Cu₄ 2969.8; UV–vis (CHCl₃) $\lambda_{max}(\varepsilon)$ =506 (105,000), 713 (65,000), and 1390 (5800) nm.

8.5. Computational method

All calculations were carried out using the Gaussian 03 program.¹⁸ All structures were optimized with Becke's three-parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP) without symmetry restriction, employing the $6-31G^*$ basis set.¹⁹ The NICS was calculated with the GIAO method at B3LYP/6-31G* level. The ring centers were designated at the nonweighted means of the carbon and nitrogen coordinates on the conjugate pathway. NMR chemical shifts were referenced to TMS (GIAO magnetic shielding tensor=32.18 ppm for protons), calculated with molecular symmetry of T_d at B3LYP/6-31G* level.

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