Expanded Porphyrins

Deutsche Ausgabe: DOI: 10.1002/ange.201505130
Internationale Ausgabe: DOI: 10.1002/anie.201505130

A Stable Organic π-Radical of a Zinc(II)–Copper(I)–Zinc(II) Complex of Decaphyrin

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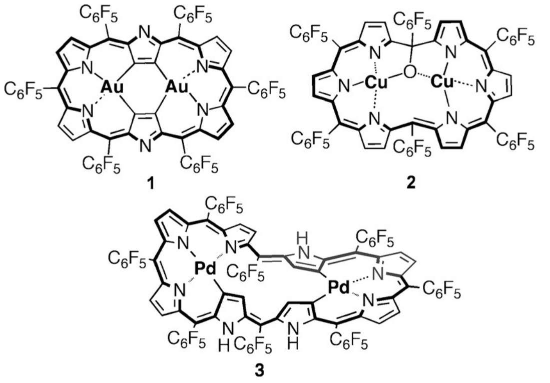
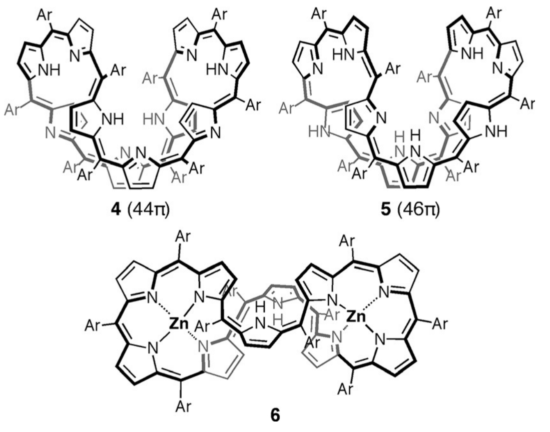
Abstract: *A Zn^{II}-Cu^{I}-Zn^{II} heterotrimetal complex of decaphyrin was synthesized by stepwise metalations: metalation of a [46]decaphyrin with Zn^{II} ions to produce a 46π decaphyrin bis(Zn^{II}) complex and its subsequent metalation with Cu^{II} ion. In the second metalation step, it has been shown that Cu^{II} ion is reduced to a Cu^{I} ion in the complex and a dianionic bis(Zn^{II}) containing [46]decaphyrin ligand is oxidized to the corresponding monoanionic [45]decaphyrin ligand, indicating a non-innocent nature of the decaphyrin ligand. Despite the radical nature, the heterotrimetal complex is fairly stable under ambient conditions and exhibits almost no intermolecular magnetic interaction, owing to extensive delocalization of an unpaired electron in the large π-conjugated circuit of decaphyrin moiety.*

Over the last two decades, expanded porphyrins have emerged as a novel class of macrocycles in light of their attractive attributes such as structural diversity, large cyclic conjugation networks, rich coordination chemistry, anion sensing abilities, and large nonlinear optical properties.[1] We have been actively involved in the chemistry of expanded porphyrins since our finding of one-pot synthesis of a series of *meso*-aryl expanded porphyrins in 2001.[2] Among many interesting features of these *meso*-aryl expanded porphyrins, their coordination chemistry is quite promising, allowing the formations of various metal complexes. These properties are arising from their fully cyclic conjugated networks having pyrrolic nitrogen atoms at regular positions, some of which can participate in metal coordination. Therefore, the structures of metal complexes of *meso*-aryl expanded porphyrins depend upon the preferred coordination geometry of a metal ion as well as the size of the expanded porphyrin. Representative examples include rectangular Au^{III} complexes of hexaphyrin **1** with multiple Au–carbon bonds,[3] gable-shaped Cu^{II} complexes of hexaphyrin **2** with notable antiferromagnetic coupling,[4] and Möbius aromatic bis(Pd^{II}) complex of octaphyrin **3** (Scheme 1).[5]



Scheme 1. Examples of metal complexes of expanded porphyrins.

Studies of *meso*-aryl expanded porphyrins become increasingly difficult upon increase in their size because of increasingly flexible conformations that lead to very complicated ^{1}H NMR spectra and chemical instabilities that are due to a decreased HOMO–LUMO energy gap. While [44]decaphyrin(1.1.1.1.1.1.1.1.1.1) **4** was formed in a low but reproducible yield (ca. 3%) in the condensation reaction of 5-(pentafluorophenyl)dipyrromethane with pentafluorobenzaldehyde (Scheme 2), its chemistry has been left almost unexplored.[6] A notable exception is our recent report on synthesis of Pd^{II} complexes of [44]- and [46]decaphyrins, which represent the largest Hückel aromatic and antiaromatic molecules, and a Möbius aromatic molecule.[7]



Scheme 2. [44]Decaphyrin **4**, [46]decaphyrin **5**, and [46]decaphyrin bis(Zn^{II}) complex **6**. ($Ar = C_6F_5$).

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201505130.

Herein, we report interesting metalation chemistry of [46]decaphyrin **5** (Scheme 2), which has six amino-type pyrrolic units and thus may accommodate three divalent metal cations in its cavity. [44]Decaphyrin **4** was reduced with $NaBH_4$ in methanol to give [46]decaphyrin **5** quantitatively. A high-resolution electrospray-ionization time-of-flight mass spectrum (HR-ESI-TOF-MS) of **5** revealed the parent ion peak at $m/z = 2435.1452$ ($[M-H]^-$, calcd for $C_{110}H_{25}N_{10}F_{50} = 2435.1471$). The structure of **5** has been confirmed by X-ray crystallographic analysis to be a C_2-symmetric crescent-like conformation (Supporting Information, Figure S7).[8] However, the ^1H NMR spectrum of **5** in $CDCl_3$ showed a complicated spectral pattern that displayed two sets of signals assignable to major and minor conformers in a ratio of 20:3, suggesting considerable conformational flexibility in solution. The major conformer showed signals at 14.76, 14.50, 14.20, 12.96, 11.97, and 6.69 ppm for the six pyrrolic NH protons and at 11.07–5.23 ppm for the pyrrolic β-protons. [46]Decaphyrin **5** is stable in the solid state but is slowly oxidized to **4** under aerobic conditions in solution.

Zn^{II} metalation of **5** was performed by refluxing its methanol solution in the presence of 5.0 equiv of $Zn(OAc)_2\cdot 2H_2O$ and 5.0 equiv of sodium acetate, which gave bis(Zn^{II}) complex **6** (Scheme 2) in 61 % yield after recrystallization from acetone and *n*-hexane. HR-ESI-TOF-MS indicated the parent ion peak of **6** at $m/z = 2558.9716$ (calcd for $C_{110}H_{21}N_{10}F_{50}{}^{64}Zn_2$ $[M-H]^-$: 2558.9741). The structure of **6** was unambiguously determined by X-ray crystallographic analysis to be a C_i-symmetric structure[9] in which the two Zn^{II} ions are coordinated with the four pyrroles (the pyrroles A, B, C, and D and the pyrroles F, G, H, and I) with bond distances of 2.031(3), 2.003(3), 1.992(3), and 2.024(3) Å for Zn−N1, Zn−N2, Zn−N3, and Zn−N4, respectively, and the central two pyrroles (pyrroles E and J) exist as a free amino-type pyrrole with a N5−N10 distance of 3.89 Å (Figure 1). The conjugation circuit of **6** is classified as an untwisted *T0* ring conformer.[1e] The largest dihedral angle in **6** is small (only 31°), which is favorable to maintain smooth conjugation over the macrocycle. The ^1H NMR spectrum of **6** indicates its symmetric structure and a diatropic ring current of the whole macrocycle by displaying downfield-shifted signals owing to the peripheral pyrrolic β-protons at 8.07, 7.93, 7.89, and 7.88 ppm (Supporting Information, Figure S2). These spectral data indicate 46π-aromatic character for **6**.[7,10]

In the next step, we tested metalation of **6** with $Cu(OAc)_2\cdot H_2O$ in the presence of sodium acetate in a mixture of methanol and ethyl acetate at room temperature for 2 h. To our delight, we obtained a decaphyrin Zn–Cu–Zn trimetal complex, **7**, in 72 % yield by simple direct recrystallization of the crude reaction mixture. HR-ESI-TOF-MS spectroscopy of **7** indicated the parent ion peak at $m/z = 2620.8885$ (calcd for $C_{110}H_{20}N_{10}F_{50}{}^{63}Cu_1{}^{64}Zn_2$ $[M]^-$: 2620.8958). The structure of **7** was determined by X-ray crystallographic analysis to be essentially the same as that of **6** except the presence of the Cu ion coordinated by the pyrroles E and J (Figure 2).[11] The Cu−N5 (Cu−N10) bond length is 1.852(3) Å and the N5-Cu-N10 angle is 180°, clearly indicating the linear bidentate coordination. The Cu−N bond of **7** is significantly shorter than those of four-coordinate Cu^I−N bonds (ca. 1.99 Å), which lies within the range of those reported for two-coordinate Cu^I−N bonds (1.84–1.89 Å).[12] Importantly, no counter anion or cation was observed in the crystal, which indicates that complex **7** is a neutral complex. The largest dihedral angle of π-conjugation circuit is 37°, which is slightly larger than that of **6** but is still small enough to maintain full conjugation over the macrocycle. The harmonic oscillator model of aromaticity (HOMA) value[13] calculated for the crystal structure of **7** is 0.54, which is almost the same as that of **6** (0.53), suggesting an effective conjugation of π-electrons.

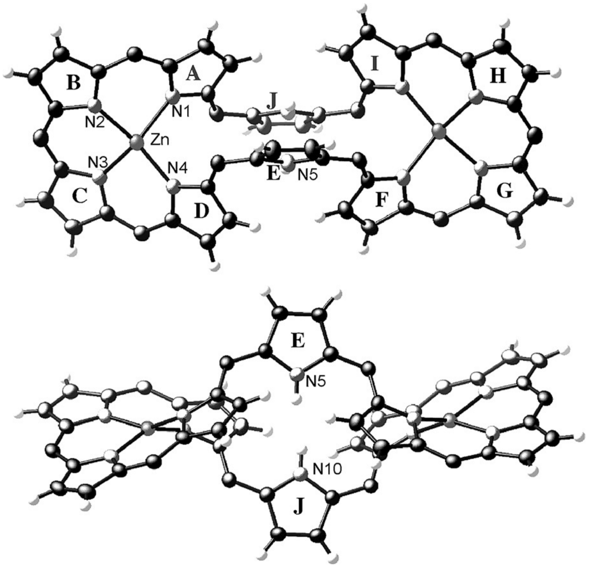


Figure 1. X-ray crystal structure of **6**. Ellipsoids are set to 50 % probability; *meso*-pentafluorophenyl substituents and solvent molecules are omitted for clarity.

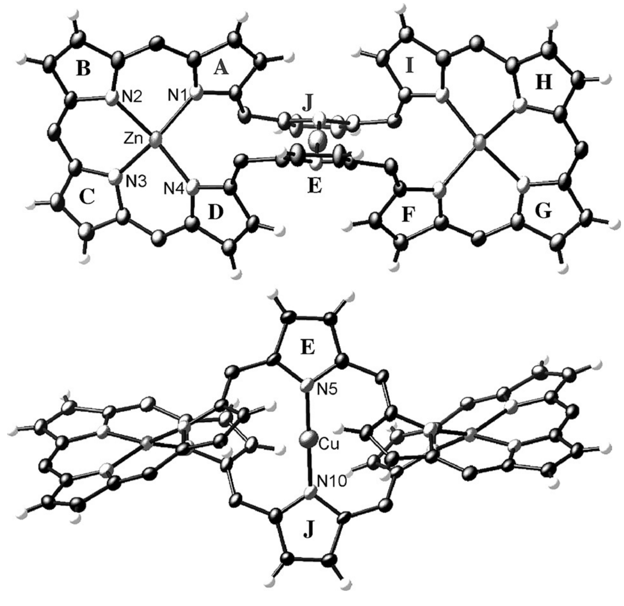
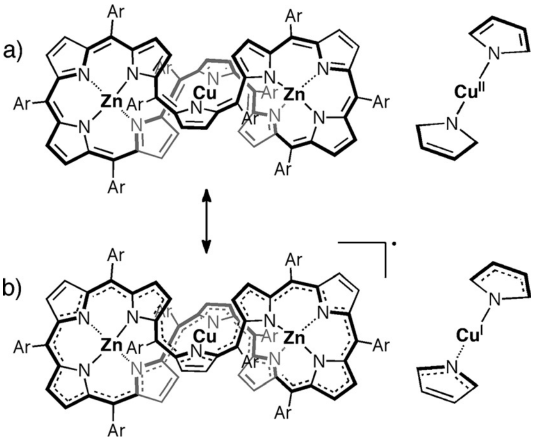


Figure 2. X-ray crystal structure of **7**. Ellipsoids are set to 50 % probability; *meso*-pentafluorophenyl substituents and solvent molecules are omitted for clarity.

At first, we conjectured that the complex **7** might be a hetero-trimetal Zn^{II}-Cu^{II}–Zn^{II} complex of [46]decaphyrin (Scheme 3 a) on the basis of its composition, molecular neutrality, and X-ray structure. However, it is hard to assume a two-coordinate linear coordinated Cu^{II} ion, since such a species would be entirely unprecedented.[14] Curiously, the ESR spectrum of **7** in frozen toluene at 20 K exhibited a relatively sharp signal with $g = 2.0177$ (Figure 3). This signal was difficult to assign as a Cu^{II} species with $S = 1/2$, since Cu^{II} species are usually observed as more broad signals, reflecting their anisotropic character. The absence of any signals in the half-field region suggested its mono-radical nature. The line width was 1.6 mT, which suggested the origin of the magnetic properties in **7** to be an organic radical. Collectively, these results strongly suggested that complex **7** is comprised of a diamagnetic Cu^{I} ion and a cation radical of [46]decaphyrin, namely a monoanionic bis(Zn^{II}) complex involving a bidentate ligand for the Cu^{I} ion that formally corresponds to a [45]decaphyrin π-conjugated electronic network (Scheme 3 b). Magnetic susceptibility measurement of **7** revealed rather constant χT values of 0.34–0.35 (emu mol^{-1}) from 10 K to 300 K, indicating very weak antiferromagnetic interaction. The observed χT values are typical of organic π-radicals (Supporting Information, Figure S12) and the weak intermolecular antiferromagnetic interaction suggested that the unpaired electron is effectively delocalized over the large π-conjugation circuit of the decaphyrin moiety. It is worth noting that complex **7** is fairly stable in the solid state or in solution under ambient conditions, despite its radical nature.



Scheme 3. Electronic resonance structure of decaphyrin ZnCuZn complex **7**: a) 46π conjugation circuit with a divalent Cu^{II} ion and b) π-radical (formal 45π conjugation circuit) with a monovalent Cu^{I} ion. (Ar = C_6F_5).

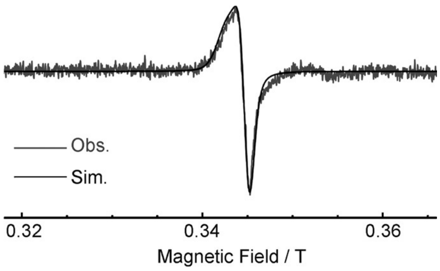


Figure 3. ESR spectrum of **7** in frozen toluene solution at 20 K.

DFT calculations at the UB3LYP/6-31G(d)//UB3LYP/LANL2DZ level[15] were performed on **7**, which indicated merely marginal spin densities on the metal centers (0.005427 for Cu ion and −0.001710 for Zn ions, Mulliken spin density), thus strongly supporting the structure of a Zn^{II}–Cu^{I}–Zn^{II} complex of a [45]decaphyrin (Figure 4). The *g* value of the complex **7** has been calculated by the GIAO methods to be 2.0032, which is in good agreement with the experimental value.

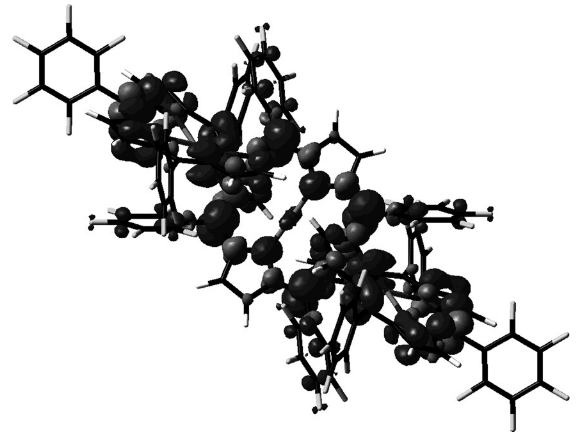


Figure 4. Calculated spin distribution of **7** calculated at the UB3LYP/6-31G(d) and LANL2DZ level. (isovalue: 0.001; the molecular geometry was optimized from the X-ray crystal structure).

The absorption spectrum of **6** shows a sharp Soret-like band at 866 nm and Q-like bands at 1308 and 1439 nm (Figure 5), which again indicates the aromaticity of the [46]decaphyrin moiety in **6**. Complex **7** also shows a slightly attenuated sharp Soret-like band at 874 nm, but Q-like bands at 1200–1500 nm are gone. Instead, a broad absorption band from 1500 to 2100 nm, probably reflecting its radical character.[16] In fact, the TD-DFT calculation indicates that the absorption band around 1500 nm originates from the SOMO→LUMO transition (Supporting Information, Fig-

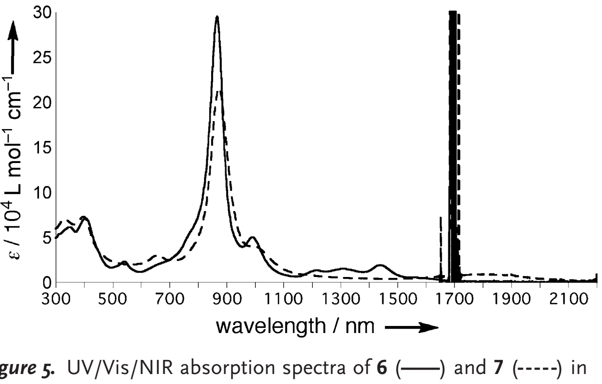


Figure 5. UV/Vis/NIR absorption spectra of **6** (——) and **7** (-----) in dichloromethane.

ure S15). The diagonal arrangement of the pyrroles E and J with a short distance of N5–N10 in **6** might be available for the coordination of Cu^{II} ion, but such a linear two-coordination structure is apparently disadvantageous for electron-deficient Cu^{II} ion, which leads to electron transfer from the decaphyrin ligand to Cu^{II} ion.

In summary, the Zn^{II}–Cu^{I}–Zn^{II} heterotrimetal complex of decaphyrin **7** was synthesized by stepwise metalations: metalation of [46]decaphyrin **5** with Zn^{II} ions to yield complex **6**, which was then metalated with $Cu(OAc)_2{\cdot}H_2O$ to give **7**. In **7**, the central copper ion has been shown to be Cu^{I} ion and the decaphyrin ligand is a monoanionic [45]decaphyrin radical, indicating a non-innocent nature of the decaphyrin ligand. Despite the radical nature, the complex **7** is fairly stable under ambient conditions and exhibits almost no intermolecular magnetic interaction, which is probably due to extensive delocalization of an unpaired electron in the large π-conjugated circuit of the decaphyrin. Further exploration of multimetal complexes of decaphyrins is actively in progress in our group.

Acknowledgements

This work at Kyoto was supported by JSPS KAKENHI Grant Numbers No. 25220802 and 25620031. We thank Takuto Kamatsuka and Satoru Ito (Nagoya University) for cyclic voltammetry measurements. Y.T., T.Y., T.K. and H.M. acknowledge a JSPS Fellowship for Young Scientists.

Keywords: copper · decaphyrin · expanded porphyrins · heterometal complexes · stable radicals

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 10908–10911
Angew. Chem. **2015**, *127*, 11058–11061

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[8] Crystallographic data of **5**: $C_{110}H_{26}N_{10}F_{50}{\cdot}(\text{acetonitrile})_5$, $M_r = 2633.61$, monoclinic, $P2_1/c$ (No. 13), $a = 16.809(3)$, $b = 23.895(4)$, $c = 27.232(5)$ Å, $\beta = 95.639(3)°$, $V = 10885(3)$ Å^3, $\rho_{calcd} = 1.607\ \text{g cm}^{-3}$, $T = 93(2)$ K, $Z = 4$, $R_1 = 0.0697$ $(I > 2.0\sigma(I))$, $wR_2 = 0.217$, GOF = 1.061.[17]

[9] Crystallographic data of **6**: $C_{110}H_{22}N_{10}F_{50}Zn_2{\cdot}(\text{acetonitrile})_{6.45}{\cdot}(\text{acetone})_{1.42}$, $M_r = 2883.33$, triclinic, $P\bar{1}$ (No. 2), $a = 13.806(7)$, $b = 14.936(5)$, $c = 15.882(6)$ Å, $\alpha = 90.0674(3)$, $\beta = 107.236(15)$, $\gamma = 100.076(17)°$, $V = 2869(2)$ Å^3, $\rho_{calcd} = 1.669\ \text{g cm}^{-3}$, $T = 93(2)$ K, $Z = 1$, $R_1 = 0.0577$ $(I > 2.0\sigma(I))$, $wR_2 = 0.1688$, GOF = 1.103.[17]

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[11] Crystallographic data of **7**: $C_{110}H_{20}N_{10}F_{50}Zn_2Cu_1{\cdot}(\text{acetonitrile})_{5.824}{\cdot}(\text{acetone})_{2.088}$ $M_r = 2955.82$, triclinic, $P\bar{1}$ (No. 2), $a = 13.718(4)$, $b = 13.983(3)$, $c = 15.774(4)$ Å, $\alpha = 90.0526(17)$, $\beta = 107.139(14)$, $\gamma = 98.009(8)°$, $V = 2859.0(13)$ Å^3, $V = 2859.0(13)$ Å^3, $\rho_{calcd} = 1.717\ \text{g cm}^{-3}$, $T = 93(2)$ K, $Z = 1$, $R_1 = 0.0684$ $(I > 2.0\sigma(I))$, $wR_2 = 0.2137$, GOF = 1.036.[17]

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[17] CCDC 1404015 (**5**), 1404016 (**6**), and 1404017 (**7**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Received: June 5, 2015