

Thermal Splitting of Bis-Cu(II) Octaphyrin(1.1.1.1.1.1.1.1) into Two Cu(II) Porphyrins

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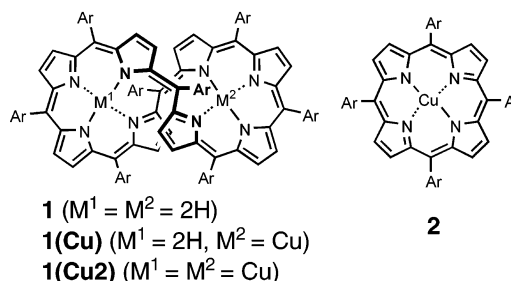
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Currently, increasing attention has been focused on the chemistry of expanded porphyrins that have pyrrolic subunits with more than four porphyrins.¹ An intriguing promise of this new class of macrocycles may be the ability to chelate two or more metal ions with the aid of large and flexible ligands. Despite this promise, there have been only scattered reports on the metalation of expanded porphyrins thus far.^{2–5} Rare interesting examples include the metalation of amethyrin³ and doubly N-confused hexaphyrin⁴ that have been shown to chelate two metal ions with notable metal–metal interactions. More recently, Vogel et al. disclosed interesting metalation behaviors of octaphyrins, in which Ni(II)-metalation of a diketo octaphyrin(1.1.1.0.1.1.1.0) induced a drastic skeletal rearrangement to a bis-Ni(II) spirodicorrole and Pd(II)-metalation of octaphyrin(1.1.1.0.1.1.1.0) triggered a different skeletal rearrangement to a bis-Pd(II) bis-spiroporphyrin.⁵ In this communication, we report the thermal splitting reaction of bis-Cu(II) complex of octaphyrin(1.1.1.1.1.1.1.1) into two Cu(II) porphyrins.

Octaphyrin(1.1.1.1.1.1.1.1) **1** was prepared by our synthesis of *meso*-aryl expanded porphyrins^{6b} (see Chart 1). In the solid-state, **1** takes a figure-eight structure with two identical porphyrin-like hemi-macrocylic tetrapyrrolic ligands that are pertinent for metal-ion coordination.^{6a} A solution of **1** in toluene was stirred at 50 °C in the presence of 10 equiv of Cu(OAc)₂ and 5 equiv of NaOAc and the metalation process was monitored by UV–vis absorption spectroscopy (Figure 1). The nonaromatic [36]octaphyrin **1** exhibited absorption bands at 410 and 643 nm, which changed to the absorption bands at 412 and 668 nm after 2 h and to the absorption bands at 351 and 522 nm after 4 h. These spectral changes have been ascribed to sequential formation of mono-Cu(II) octaphyrin **1(Cu)** and bis-Cu(II) octaphyrin **1(Cu2)**, by referring to the respective authentic absorption spectra. To our surprise, the absorption spectrum of this reaction mixture changed dramatically upon prolonged stirring and after 2 weeks finally displayed an absorption spectrum with a sharp band at 408 nm and two small bands at 535 and 570 nm. The final spectrum apparently indicated the formation of Cu(II) porphyrin **2** that was actually isolated in 67% yield from this reaction mixture. Elevating the reaction temperature to 111 °C (refluxing toluene) completed the splitting reaction within 2 h, providing **2** in 91% yield.

Copper complexes **1(Cu)** and **1(Cu2)** were prepared under controlled metalation conditions in 77 and 81% yields, respectively (Supporting Information).⁷ With pure **1(Cu2)** in hand, the activation parameters of the splitting reaction were determined. The splitting reaction of **1(Cu2)** was found to be an unimolecular process with $\Delta H^\ddagger = 68.2$ kJ/mol and $\Delta S^\ddagger = -133$ eu.⁸ Despite the dissociative nature of the splitting reaction, the observed large negative activation entropy is notable, since it suggests a greater degree of

Chart 1. Ar = Pentafluorophenyl



ordering in the transition state than the initial state. The reaction rates were virtually not influenced upon the increase of solvent polarity, $2.3 \times 10^{-4} \text{ s}^{-1}$ in nonpolar toluene and $2.2 \times 10^{-4} \text{ s}^{-1}$ in polar DMF at 100 °C, suggesting only a small polarity change in the transition state compared to the starting substrate **1(Cu2)**. More importantly the splitting reaction has not been observed either for **1** or for **1(Cu)** even for prolonged refluxing in toluene solutions, highlighting the crucial importance of two Cu(II) ion coordination in **1** for the splitting reaction. We have tested the metalation of **1** with a variety of metal ions with a view to find the similar splitting reaction and have found that the formation of porphyrin derivatives was noted in small amounts for some metals such as Pd(II), Co(II), and Ni(II) ions, but the quantitative splitting into two porphyrins was only observed for Cu(II) ion.

X-ray diffraction analysis of **1(Cu2)** reveals C_2 symmetry of the molecule and the presence of two copper atoms centrally bound within the core of a severely distorted octaphyrin macrocycle (Figure 2).⁹ Two copper atoms are both coordinated with a porphyrin-like hemi-macrocylic ligand with Cu–N1, Cu–N2, Cu–N3, and Cu–N4 bond distances being 2.06, 1.97, 1.98, and 2.02

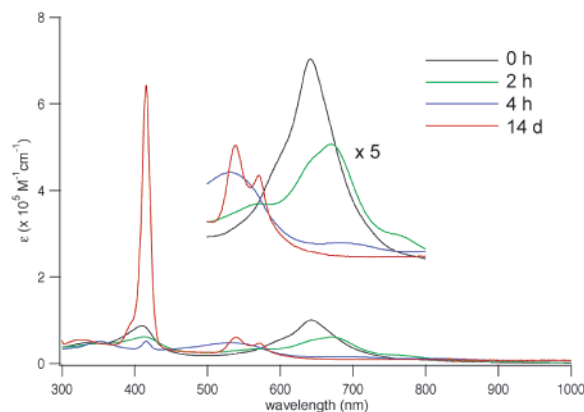


Figure 1. UV–vis absorption spectra recorded during the metalation of **1** with Cu(OAc)₂ at 50 °C in toluene.

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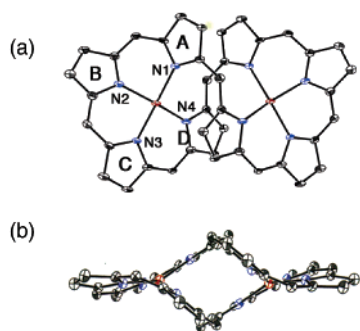
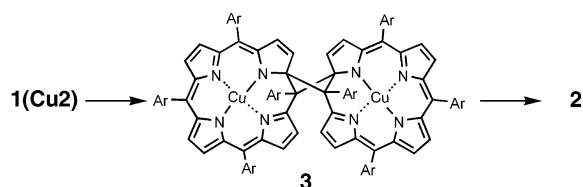


Figure 2. X-ray structures of **1(Cu2)**. (a) Top view and (b) side view. The thermal ellipsoids were scaled to the 50% probability level. Hydrogen atoms and pentafluorophenyl substituents are omitted for clarity.

Å, respectively, and the Cu–Cu distance is 5.42 Å. A tripyrrolic unit consisting of pyrroles B, C, and D is relatively flat with the mean-plane deviation of 0.17 Å, while the pyrrole A plane is tilted by 63° with respect to the above plane and the Cu atom is displaced out of this plane by 0.757 Å. Collectively, the coordinating structure of **1(Cu2)** is severely distorted, which is in sharp contrast to the porphyrin **2** that exhibits a quite planar structure as shown by its X-ray structure with the mean plane deviation of only 0.015 Å (Supporting Information).¹⁰ These features suggest that the relief of strain in **1(Cu2)** may be a main driving force for this thermal splitting reaction. We thus examined the thermal behavior of **1(Cu2)** by differential scanning calorimetry (DSC) at a rate of 25 °C/min, which revealed a sharp exothermic response between 240 and 280 °C, and the porphyrin **2** was obtained in high yield from this thermolysis experiment. Such a response was not observed for either **1** or **1(Cu)**. From the DSC experiment, the formation energy of **2** was estimated to be 135 kJ/mol, which can be considered to arise from a stability difference between **1(Cu2)** and **2**. One possible mechanism of the splitting reaction may be $2\pi + 2\pi$ cycloaddition to give spirocyclobutane intermediate **3**, which is split into two molecules of **2** via a cycloreversion reaction.



The present thermal splitting reaction of **1(Cu2)** to **2** may be attractive also for application to a recording device in terms of the dramatic spectral changes as well as the perfect material balance. We thus examined the similar splitting reaction of **1(Cu2)** in a film state. Fortunately, **1(Cu2)** was found to form a good transparent film by spin coating of its 2% toluene solution (500 rpm, 10 s and 2000 rpm, 60s) onto the quartz. In the film state, **1(Cu2)** exhibited broad bands at 354, 531, and 693 nm due to aggregation and was more robust than in solution, being stable under 140 °C. Heating

the film of **1(Cu2)** at 200 °C, however, gave rise to clean splitting into **2** as judged from newly appearing absorption bands, 413 (Soret), 537 (Q), and 573 (Q) nm, encouraging the use of this process in patterned FET and thermal/optical recording/reading devices.

As demonstrated above, the Cu(II) metalation of octaphyrin-(1.1.1.1.1.1.1.1) gave rise to the facile splitting reaction triggered by increased distortion in the bis-metal complex **1(Cu2)**, which provided a rare example of “molecular mitosis” for expanded porphyrins.¹¹ Studies on the metalation of other *meso*-aryl expanded porphyrins are actively in progress to explore their novel reactivities and potentials.

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Supporting Information Available: Synthetic procedures and spectral data of **1(Cu)** and **1(Cu2)**, absorption spectral changes of **1(Cu2)** during heating in the film state, Arrhenius and Eyring plots, DSC experiments. CIF files for the X-ray structural analysis of **1(Cu2)** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (7) **1(Cu)** and **1(Cu2)** showed the parent ion peaks at $m/z = 2009.0444$ (calcd for $C_{88}H_{18}N_8F_{40}Cu$, 2009.0412) and $m/z = 2069.9668$ (calcd for $C_{88}H_{16}N_8F_{40}Cu_2$, 2069.9651), respectively.
- (8) The Arrhenius plot provided a preexponential factor of $2.2 \times 10^6 s^{-1}$ and an activation energy of 71.1 kJ/mol.
- (9) **1(Cu2)**: $C_{92}H_{21}N_8O_{10}F_{40}Cu_2$, $M_w = 2285.25$, P_{bcn} , with $a = 23.140(3)$ Å, $b = 15.364(2)$ Å, $c = 24.814(3)$ Å, $V = 8822(1)$ Å³, $Z = 4$, $\mu = 6.303$ cm⁻¹, $D_{calc} = 1.693$ g/cm³, and crystal dimensions 0.80 mm × 0.40 mm × 0.20 mm. The data were collected on Bruker SMART diffractometer at -153 °C, and the structure was solved by direct methods. It was refined to $R = 0.077$, $R_w = 0.096$, GOF = 1.058 for 6433 with $I > 3.0 \sigma(I)$.
- (10) The mean plane deviation of **2** was previously reported to be 0.032 Å. Birnbaum, E. R.; Hodge, J. A.; Grinstaff, M. W.; Schaefer, W. P.; Henling, L.; Labinger, J. A.; Bercaw, J. E.; Gray, H. B. *Inorg. Chem.* **1995**, *34*, 3625.
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