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Self-assembly of Zn(II) Porphyrin–1,2,3-Triazole Conjugate with Alcohol Glue

Motoki Toganoh,[1] Hiroyuki Harada,[1] Yoshiya Ikawa,[1,2] and Hiroyuki Furuta*[1]
[1]*Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University,*
744 Motooka, Nishi-ku, Fukuoka 819-0395
[2]*PRESTO, Japan Science and Technology Agency (JST), Tokyo 102-0075*

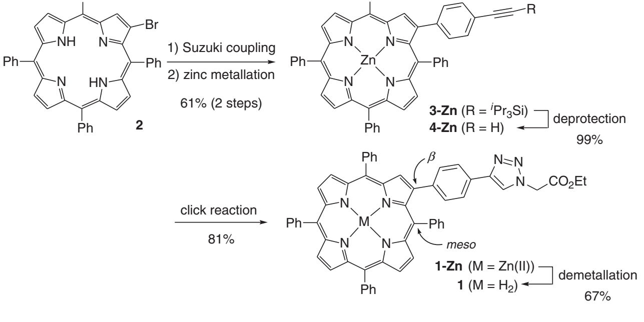
(Received December 28, 2009; CL-091152; E-mail: hfuruta@cstf.kyushu-u.ac.jp)

A Zn(II) porphyrin–1,2,3-triazole conjugate (**1-Zn**), which can be prepared by click chemistry, afforded a unique self-assembled structure with methanol molecules as glue in the crystals and in toluene solution. The resulting assembled units form a zigzag architecture due to multipoint CH–π interactions in the solid state.

Click chemistry has been widely used in construction of a variety of conjugated molecules.[1,2] Although a major role of click chemistry is just connecting two building blocks, the resulting bridge part, a 1,2,3-triazole unit, is sometimes used for metal coordination. For example, a 1,2,3-triazole-appended zinc(II) porphyrin formed a self-assembled dimer[3] and conjugates of a biomolecule and a transition-metal complex were readily prepared by the click reactions.[4,5] In addition to these *N*-coordinated complexes, the application of a 1,2,3-triazole ring to *C*-coordinated complexes or *N*-heterocyclic carbene complexes was also reported.[6]

Alternatively, a 1,2,3-triazole unit can serve as a hydrogen-bonding acceptor or donor. Although molecular recognition or the construction of supramolecules through hydrogen bondings with a 1,2,3-triazole unit can be expected, such examples are hardly ever reported. This time we have prepared a new type of 1,2,3-triazole-appended zinc(II) porphyrin and studied its assembly. While direct self-recognition through metal coordination was not observed certainly due to the steric hindrance, formation of a 2:2 assembled structure between the zinc(II) porphyrin–1,2,3-triazole conjugates (**1-Zn**) and methanol molecules was observed unexpectedly, where the methanol molecules work as glue through hydrogen bondings as well as metal coordination.

The zinc(II) porphyrin–1,2,3-triazole conjugate (**1-Zn**) was prepared in four steps from the β-bromotetraphenylporphyrin (**2**)[7] as shown in Scheme 1. The Suzuki cross coupling reaction of **2** with 4-[(triisopropylsilyl)ethynyl]phenylboronic acid[8] and subsequent zinc metalation gave the β-arylated Zn(II) porphyrin (**3-Zn**) in 61% yield (2 steps). Then, deprotection of **3-Zn** with Bu$_4$NF gave the terminal alkyne (**4-Zn**) in 99% yield and the click reaction of **4** with an ethyl azidoacetate gave the Zn(II) porphyrin–1,2,3-triazole conjugate (**1-Zn**) in 81% yield. The free base form **1** was also prepared by demetalation of **1-Zn** with CF$_3$CO$_2$H in 67% yield.



Scheme 1. Synthesis of **1-Zn**.

The ^{1}H NMR spectra of **1** and **1-Zn** in CDCl$_3$ (or toluene-d_8) closely resemble each other except for the signal due to the inner NH protons at -2.61 ppm and the high-field shifts of the porphyrin β-protons by ca. 0.1 ppm in **1**, suggesting **1-Zn** alone does not form any self-recognized oligomers in solution (Figure S1).[9] For example, the signals assignable to the 1,2,3-triazole moiety appeared at 7.93 (**1**) and 7.94 ppm (**1-Zn**). The signals due to the β-phenylene moiety were observed at 7.40, 7.62 ppm for **1** and 7.41, 7.62 ppm for **1-Zn**. Note that the porphyrin derivatives possessing a coordination group at the *meso*- or β-positions often afford the self-recognized oligomers, where the distinct low-field shifts of some signals are observed due to the shielding effect of a paired [18]annulenic porphyrin macrocycle.[3,10–12] The absence of oligomer formation can be explained by steric factors. Namely, access to the center zinc metal by the triazole nitrogen atom of another molecule is blocked by the β-phenylene and CH$_2$CO$_2$Et groups.

Although **1-Zn** alone did not form any oligomeric structures, it formed a 2:2 assembled structure with CH$_3$OH, which was demonstrated by X-ray crystallographic analysis (Figure 1). Thus, **1-Zn** was recrystallized from CH$_2$Cl$_2$/CH$_3$OH to give red plates, one of which was subjected to X-ray analysis.[13] The oxygen atom of a CH$_3$OH molecule coordinates to the zinc(II) metal (Zn–O: 2.149 Å) of a porphyrin conjugate and the hydroxy proton of the same CH$_3$OH molecule forms hydrogen bonding with the 1,2,3-triazole unit of another porphyrin conjugate (O–N: 2.749 Å). As a result, a 2:2 assembled structure was constructed with **1-Zn** and CH$_3$OH. Furthermore, two porphyrin conjugates interact with each other by multipoint CH–π interactions, where the distances between the porphyrin mean plane composed of 24 heavy atoms and the aryl protons are 2.40–2.75 Å on the assumption of C–H bond length being 0.93 Å (Figure 1b). Interestingly, synergy of these interactions resulted in the formation of the aligned zigzag structures in a solid state (Figure 1c).

The variable temperature ^{1}H NMR analysis of **1-Zn** in the presence of CH$_3$OH implied the formation of the 2:2 assembled structures even in solution (Figures 2 and S2). By cooling **1-Zn** and CH$_3$OH (3.4 equiv) in toluene-d_8 from 20 to -20 °C, high-field shifts of the signals due to CH$_3$OH were observed, which would be explained by coordination of CH$_3$OH to the center metal of **1-Zn**. The signals due to the β-phenylene moiety did not shift significantly at this stage. Meanwhile, one of the two β-phenylene signals showed distinct high-field shifts by further

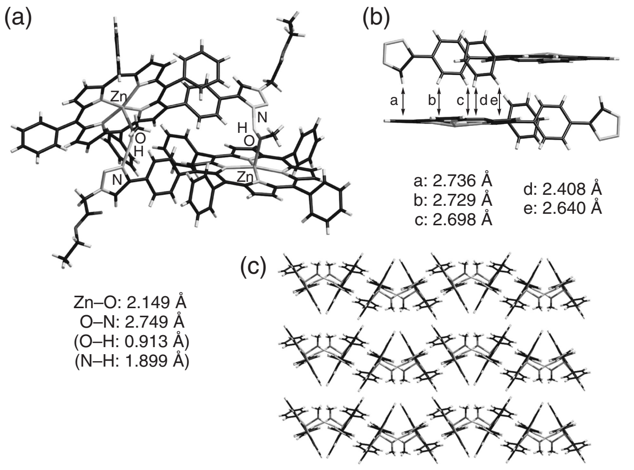


Figure 1. X-ray structures of **1-Zn**·CH_3OH: (a) 2:2 assembled structure by the hydrogen bondings, (b) CH–π interactions between porphyrin plane and aryl groups, and (c) packing diagram in the solid state. The phenyl groups at the 5, 10, and 15 positions and the CH_2CO_2Et group are omitted for clarity in (b) and (c).

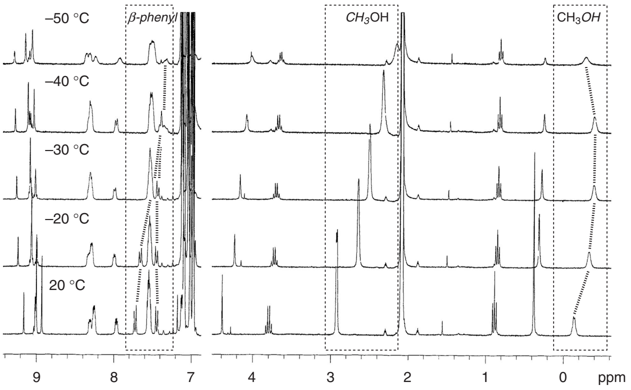
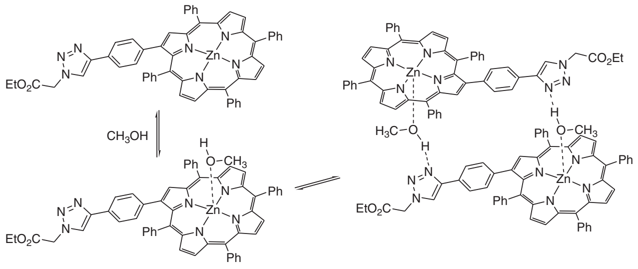


Figure 2. Variable temperature ^1H NMR spectra of **1-Zn** with 3.4 equiv of CH_3OH in toluene-d_8.

cooling from −20 to −50 °C. Additionally, the high-field shifts of the hydroxy proton of the methanol became smaller or even the low-field shifts were observed. This behavior can be explained by the formation of the 2:2 assembled structures. The former would be rationalized by the shielding effect imposed by the paired porphyrin macrocycle and the latter might be due to the hydrogen bonding of the hydroxy proton with the 1,2,3-trizaole moiety. The formation of 2:2 assembled structures was also inferred from the severe broadening of the signals at lower temperature. In contrast, only the large high-field shifts of the CH_3OH protons were observed when similar ^1H NMR measurements were achieved on **3-Zn** (Figure S3). The signals due to the β-phenylene moiety of **3-Zn** did not shift significantly unlike **1-Zn**. The characteristic shifts like Figure 2 were not observed in CD_2Cl_2, meaning the importance of less polar solvents in the solution phase assembly. The observation of only one set of the signals due to CH_3OH even under the presence of excessive amounts suggested the rapid equilibrium between the monomer and the dimer in the NMR time scale (Scheme 2). Obviously, the initial NMR spectrum was obtained again upon heating the chilled solution to ambient temperature.



Scheme 2. Formation of a 2:2 assembled structure with **1-Zn** and CH_3OH.

In summary, we have synthesized a zinc(II) porphyrin–1,2,3-triazole conjugate, in which a unique 2:2 assembled structure with CH_3OH was observed in the solid state and most likely in toluene solution.[14] This work demonstrates the applicability of a 1,2,3-triazole unit formed by a click reaction to a hydrogen-bonding acceptor and further application of the click chemistry in supramolecular chemistry based on hydrogen bondings will be expected.

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13 Crystal data: **1-Zn**·CH_3OH, red plate, $C_{57}H_{43}N_7O_3Zn$, $M_r = 939.35$, monoclinic, space group $C2/c$ (No. 15), $a = 42.603(5)$, $b = 10.2888(12)$, $c = 21.811(3)$ Å, $\beta = 105.962(2)°$, $V = 9192(2)$ Å^3, $Z = 8$, $T = 296(2)$ K, $R = 0.0583$ ($I > 2\sigma(I)$), $R_w = 0.1783$ (all data), GOF = 0.895, CCDC number 743205.
14 Experiments with ethanol and 2-propanol in place of methanol did not give clear evidence for formation of 2:2 assembled structures so far.