

Bay-Area Selective Thermal [4+2] and [4+4] Cycloaddition Reactions of Triply Linked Zn^{II} Diporphyrin with *o*-Xylylene

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Abstract: A triply linked Zn^{II} diporphyrin underwent site-selective cycloaddition reactions with thermally generated *o*-xylylene to provide a triply linked porphyrin–chlorin hybrid and a triply linked chlorin dimer in moderate yields. The former product is a symmetry-allowed [4+2] cycloadduct, while the latter is a symmetry-forbidden [4+4] cycloadduct. Oxidation of the latter product with 2,3-dichloro-5,6-di-

cyano-1,4-benzoquinone (DDQ) provided a triply linked diporphyrin fused with a benzocyclooctatriene segment. This oxidized product and above [4+2] cycloadduct were structurally characterized by single crystal X-ray diffraction

Keywords: cycloaddition · porphyrinoids · site-selectivity · X-ray diffraction

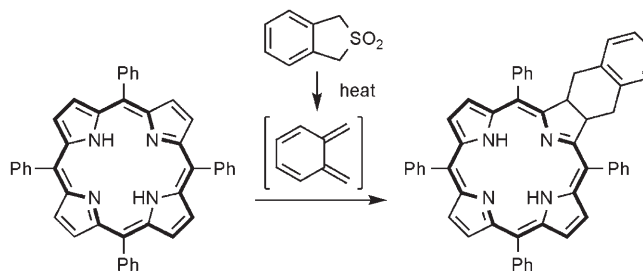
tion analysis. The observed site-selectivity is considered to arise from the large MO coefficients at the bay-area in the LUMO of the triply linked diporphyrin. The anomalous thermal [4+4] cycloaddition may be ascribed to the highly conjugated and quite perturbed electronic properties of triply linked Zn^{II} diporphyrin.

Introduction

Recently considerable attention has been focused on the exploration of extensively π -conjugated porphyrins in light of their potential applications in optoelectronic devices, sensors, photovoltaic devices, nonlinear optical materials, photodynamic therapy pigments, and so forth.^[1–10] Among these, we have explored the *meso*–*meso*, β – β , β – β triply linked porphyrin arrays (porphyrin tapes) that display remarkably red-shifted absorption bands due to the extensive electronic delocalization.^[11] The planar molecular frameworks and full electronic conjugation of the porphyrin tapes are appealing in that they exhibit unique electrochemical and optical properties, such as large two-photon absorption cross sections,^[12] extremely short-lived singlet excited states,^[13,14a] fluorescence in the near-infrared region,^[13,14a] multicharge storage,^[14b] and electronically communicative guest binding.^[15] Thus, chemical modifications of the electronic systems of porphyrin tapes at their peripheries would be useful to create novel π -conjugated functional porphyrins but the

chemical reactivities of these molecules have remained almost unexplored and there have been only a few reports on the chemical transformations of porphyrin tapes.^[16]

Herein, we report the cycloaddition reaction of a triply linked Zn^{II} diporphyrin with *o*-xylylene. It has now been well recognized that porphyrin peripheries are reactive toward dienes and 1,3-dipoles and porphyrins undergo concerted Diels–Alder reactions and 1,3-dipolar cycloaddition reactions under appropriate reaction conditions. Many interesting cycloaddition reactions of porphyrins were reported by Cavaleiro et al.^[17] Scheme 1 shows a typical example of the reaction of *meso*-tetraphenyl porphyrin with *o*-xylylene.^[17a] A porphyrin has an 18 π -conjugated aromatic electronic system and the peripheral diagonal pyrrolic double bonds are partially isolated from this aromatic conjugation

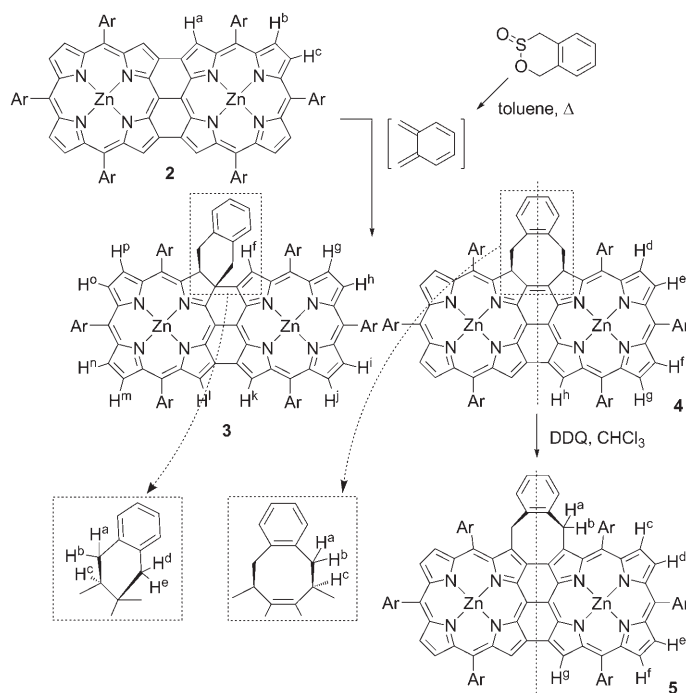


Scheme 1. Aromatic electronic network of *meso*-tetraphenyl porphyrin and its Diels–Alder reaction with *o*-xylylene.

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pathway. This explains the reactivity of the peripheral double bonds of porphyrin. Recently, similar cycloaddition reactions were also disclosed for *meso*-aryl-substituted expanded porphyrins, such as aromatic [26]hexaphyrin(1.1.1.1.1.1) and nonaromatic [36]octaphyrin(1.1.1.1.1.1.1.1).^[18] These concerted cycloaddition reactions are considered to proceed by means of orbital interactions between a diene (or a 1,3-dipole) and a pyrrolic double bond of porphyrin as a dienophile (or a 1,3-dipolarophile).^[19] In this respect, triply linked diporphyrins that have considerably perturbed and highly conjugated electronic systems are particularly attractive, as they may show different reactivities from normal porphyrins. In addition, it is expected that the extremely small HOMO–LUMO gaps of triply linked diporphyrins may facilitate the cycloaddition reaction, as the frontier orbitals that will interact most and overlap best and are those that are closest in energy.^[19] With this in mind, we examined the reaction of triply linked diporphyrin **2** with *o*-xylylene and found that the cycloaddition occurs site-selectively at the bay area of the triply linked diporphyrin, and, quite unexpectedly, along with a symmetry allowed [4+2] cycloadduct, a symmetry forbidden [4+4] cycloadduct was formed in moderate yield Scheme 2.



Scheme 2. Cycloaddition reaction of **2** and *o*-xylylene. Ar = 3,5-di-*tert*-butylphenyl.

Results and Discussion

Triply linked Zn^{II} diporphyrin **2**, which bears *meso*-(3,5-di-*tert*-butylphenyl) substituents was employed as a substrate for the cycloaddition reaction with *o*-xylylene because of its nice solubility and high structural symmetry. A solution of **2** (1 equiv) and benzosultine^[20] (1.5 equiv) in toluene was re-

fluxed under a nitrogen atmosphere. Under these conditions, the reaction was found to proceed slowly to afford two products **3** and **4** both in less than 5% yields together with recovered **2** (>60%) after 3 h. The products **3** and **4** were separated as a pinkish purple fraction and a green fraction, respectively, by silica-gel column chromatography. Compounds **3** and **4** exhibited the parent ion peaks at $m/z = 1976.0372$ (calcd for C₁₃₂H₁₄₇N₈Zn₂: 1976.0343 [M+H]⁺) and at $m/z = 1975.0168$ (calcd for C₁₃₂H₁₄₆N₈Zn₂: 1975.0254 [M]⁺) in the high-resolution electrospray-ionization time-of-flight (HR-ESI-TOF) mass spectra. These results indicate that both products are 1:1 adducts of **2** with *o*-xylylene. In the meantime, we found that successive additions of 0.5 equivalents of benzosultine every 15 minutes (14 times, total 7 equiv) to a toluene solution of **2** improved yields and allowed us to isolate **3** and **4** in 21 and 15% yields along with recovered **2** (37%). Further addition of benzosultine and prolonged heating led to formation of a complicated mixture.

The structures of **3** and **4** were determined by the analyses of their ¹H NMR spectra. The ¹H NMR spectrum of **2** in CDCl₃ is relatively simple, featuring a pair of mutually coupled doublets at $\delta = 7.74$ and 7.70 ppm with $J = 4.7$ Hz due to the side β protons, a singlet at $\delta = 7.35$ ppm due to the inner β protons, and four signals due to the aromatic protons of the *meso*-(3,5-di-*tert*-butylphenyl) substituents in line with its D_{2h} symmetric molecular structure. The characteristically shielded signals due to the β protons of **2** have been interpreted in terms of a weakened diatropic ring current of the triply linked diporphyrin.^[11] The ¹H NMR spectrum of **3** in C₆D₆ is rather complicated, exhibiting eight mutually coupled doublets due to the side β protons, with three singlets at $\delta = 9.15$, 8.95, and 7.71 ppm due to the inner β protons (Hⁱ or H^k, and H^f), eighteen signals due to the aromatic protons in the *meso*-aryl substituents, and two doublets (H^d + H^e) and two double doublets (H^a + H^b) due to the benzylic methylene protons. The COSY measurement showed the correlation between the signals due to H^a and H^b and the triplet at $\delta = 5.85$ ppm, thus allowing us to assign the latter peak to H^c (Figure 1). The observed chemical shift of H^c is

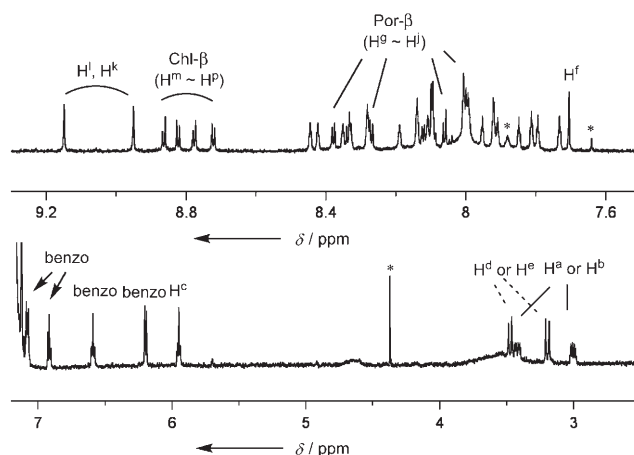


Figure 1. ¹H NMR spectrum of **3** in [D₆]benzene (* indicates impurity).

similar to that ($\delta=5.32$ ppm) of the corresponding β protons of porphyrin-*o*-xylylene cycloadduct **1**. The doublet signals of the peripheral β protons of **3** can be classified into two groups with ranges of $\delta=8.90$ – 8.70 and 8.40 – 8.00 ppm. These different chemical shifts can be interpreted in terms of different ring currents of the porphyrin and chlorin subunits in **3**. We assigned the signals in the range of $\delta=8.90$ – 8.70 ppm to those of the chlorin-type subunit and those in the range of $\delta=8.40$ – 8.00 ppm to those of the porphyrin-type subunit on the basis of a comparison with the signals of **2**, **4**, and **5** (vide infra). Overall the ^1H NMR spectrum of **3** clearly indicates no symmetry in its molecular structure and supports the assigned structure. Figure 2 shows the struc-

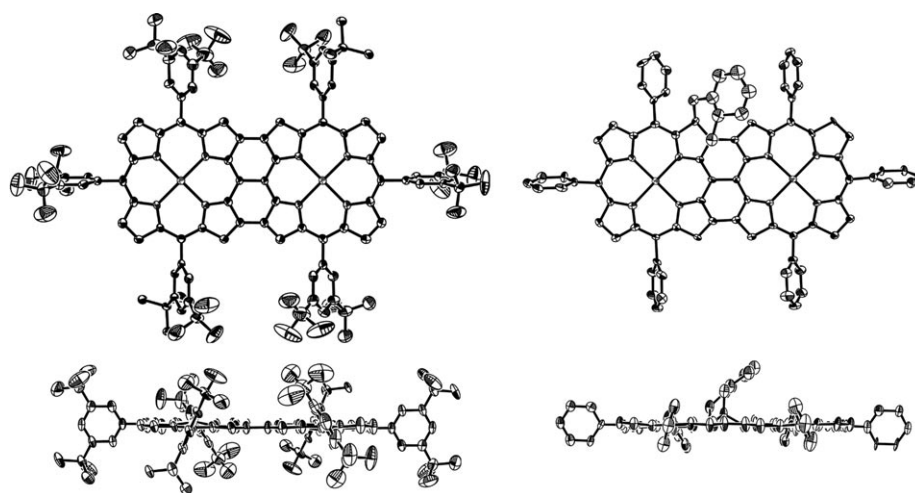


Figure 2. ORTEP presentations of X-ray crystal structures of **2** (left) and **3** (right). Top is a top view and bottom is a side view (thermal ellipsoids 50% probability). Hydrogen atoms, *tert*-butyl substituents in **3**, and coordinating solvents were omitted for clarity.

tures of **2** and **3** as determined by single-crystal X-ray diffraction analyses. In line with the previous report,^[11d] the structure of **2** is planar and rectangular. The mean plane deviation defined by the core 48 atoms is 0.050 Å, and the rectangular shape is defined by 6.9×15.3 Å wide. The structure of **3** has been determined to be similarly flat and rectangular shaped with a small mean plane deviation of 0.051 Å, but differs distinctly due to the presence of a benzocyclohexane segment fused at the bay area with a dihedral angle of 31.1° . Another important piece of structural information revealed by the X-ray structure is that **3** is an *exo*-addition product, protruding the benzocyclohexane segment to the outside of the diporphyrin core.

The ^1H NMR spectrum of **4** (Figure 3) in CDCl_3 is simpler than that of **3**, exhibiting two pairs of mutually coupled doublets due to the side β protons (H^d , H^e , H^f , and H^g , Scheme 2) at $\delta=8.40$ and 8.21 ppm and $\delta=8.31$ and 8.18 ppm, a singlet due to the inner β protons (H^h) at $\delta=9.17$ ppm, nine signals due to the aromatic protons in the *meso*-aryl substituents, a pair of doublets due to the aromatic protons in the fused benzene ring at $\delta=6.95$ and 5.83 ppm, a double doublet signal due to the H^c -methine

protons at $\delta=6.17$ ppm, and a pair of double doublets due to the benzylic protons (H^a and H^b) at $\delta=3.88$ and 3.28 ppm with $J=13.8$ Hz (Figure 2). These ^1H NMR spectral data are in full agreement with the structural assignment of this product as **4** with C_s symmetry. Therefore, it has been concluded that the product **4** is a formal [4+4] cycloaddition product of **2** and *o*-xylylene. This assigned structure has also been supported by its preliminary X-ray crystal analysis (see the Supporting Information). The formation of **4** is of mechanistic interest, as [4+4] cycloaddition is thermally forbidden and only proceeds with the aid of photochemical activation or transition-metal catalysts.^[21]

In the next step, the oxidation of **4** was attempted. Treatment of **4** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in CHCl_3 for 1 h gave compound **5** in 86% yield. The HR-ESI-TOF mass spectrum of **5** exhibits the parent-ion peak at $m/z=1973.0148$ (calcd for $\text{C}_{132}\text{H}_{144}\text{N}_8\text{Zn}_2$: 1973.0097 [M]⁺) indicating a loss of two hydrogen atoms from **4**. The ^1H NMR spectrum of **5** in CDCl_3 is too broad to analyze at room temperature but becomes sharp enough for the assignment at -60°C and exhibits two pairs of doublets ($J=4.6$ Hz) at $\delta=7.84$ and 7.77 ppm and ($J=4.6$ Hz) at $\delta=7.82$ and 7.69 ppm due to the β protons (H^e , H^d , H^e , and H^f ,

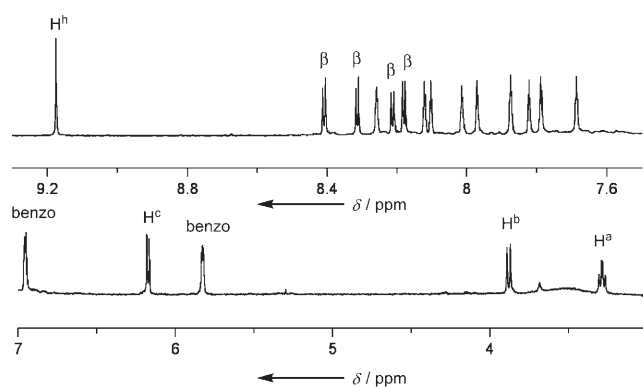


Figure 3. ^1H NMR spectrum of **4** in CDCl_3 .

Scheme 2), a singlet at $\delta=7.39$ ppm due to H^g , a pair of mutually coupled doublets ($J=15.6$ Hz) at $\delta=4.18$ and 2.98 ppm due to the benzylic protons (H^a and H^b), a pair of double doublets at $\delta=6.99$ and 6.82 ppm due to the aromatic protons of the fused benzene ring, and nine signals due to the aromatic protons of the *meso*-(3,5-di-*tert*-butylphenyl) substituents (Figure 4). These data are fully in agreement

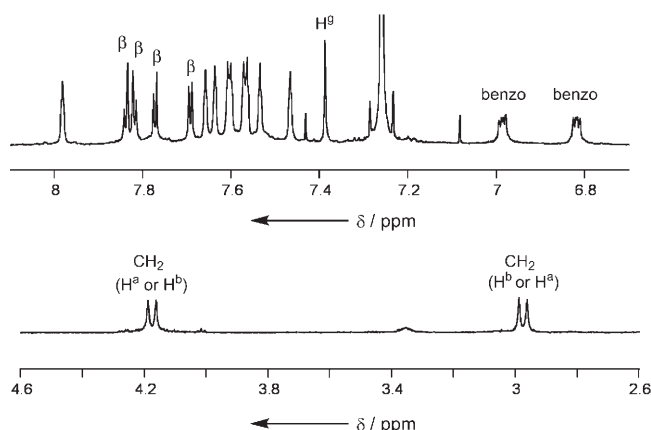


Figure 4. ^1H NMR spectrum of **5** in CDCl_3 at -60°C .

with the structure of **5**, a dehydrogenation product from **4**. It is interesting to note that a triply linked Zn^{II} diporphyrin framework is restored in **5**, and an upfield shifted signal of H^{e} relative to H^{h} of **4** indicates a similar π -electronic network to that of **2**.

Crystals of **5** that are suitable for its X-ray analysis were obtained by slow vapor diffusion of 2-propanol into 1,2-dichloroethane solution. The structure of **5** was unambiguously determined by single-crystal X-ray diffraction analysis as shown in Figure 5. The triply linked diporphyrin skeleton takes almost the same shape as that of **2**; a flat rectangular shape of $6.9 \times 15.4 \text{ \AA}$ size with the mean plane deviation of 0.076 \AA , to which the benzocyclooctatriene segment is fused almost perpendicularly with a dihedral angle of 84° , probably to mitigate steric repulsion with neighboring *meso*-(3,5-di-*tert*-butylphenyl) substituents.

Further oxidation (dehydrogenation) of **5** was also examined to prepare a cyclooctatetraene (COT)-fused triply linked Zn^{II} diporphyrin, as COT-fused porphyrinoids display quite unique electronic properties.^[10c,d] Oxidations of **5** with DDQ under more forceful conditions and by the combined use of DDQ and $\text{Sc}(\text{OTf})_3$ under various conditions were attempted without success, all giving complicated mixtures. We reasoned that these failures were due to the easily oxidized nature of triply linked Zn^{II} diporphyrin and examined the oxidation reaction of the corresponding Ni^{II} complex which is known to have a higher oxidation potential.^[11d] However, this attempt also failed, giving complicated reaction mixtures under various conditions.

Figure 6 shows the UV/Vis absorption spectra of **2**, **3**, **4**, and **5** in CHCl_3 . The absorption spectrum of **2** is typical of triply linked Zn^{II} diporphyrins, con-

sisting of three bands: a Soret-like band arising from a π - π^* transition along the short molecular axis around $\lambda = 400 \text{ nm}$ (band I), a Soret-like band along the long molecular axis at around $\lambda = 600 \text{ nm}$ (band II), and Q-band-like bands at $\lambda = 700$ – 1100 nm (bands III) that are intensified as a result of the breakage of the high molecular symmetry of a porphyrin monomer.^[13] Upon elongation of porphyrin tapes, band I remains at the same position but bands II and III are progressively red-shifted.^[11b] In contrast, the absorption spectra of **3** and **4** are ill-defined, exhibiting bands at $\lambda = 412, 486, 579,$ and 820 nm and $\lambda = 429, 503, 625,$ and 729 nm , respectively. Here it should be noted that dimers **3** and **4** are, to the best of our knowledge, the first examples of a directly triply linked porphyrin–chlorin hybrid dimer and a chlorin dimer. The Q-band-like bands are not significantly red-shifted in **4**, while those in **3** are red-shifted in a similar manner to those

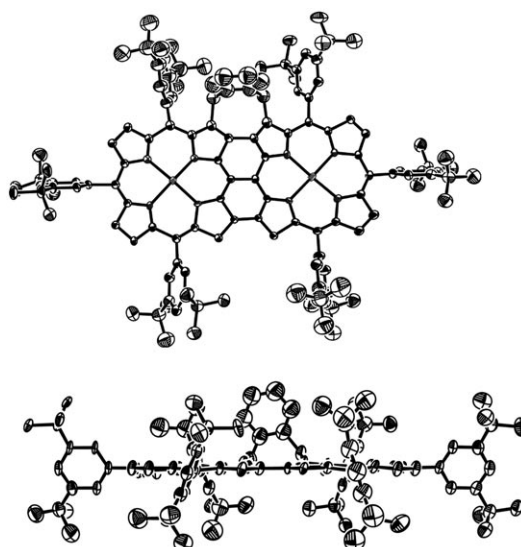


Figure 5. ORTEP presentation of the X-ray crystal structure of **5**. Top is a top view and bottom is a side view (thermal ellipsoids 50% probability). Hydrogen atoms and coordinating solvents were omitted for clarity.

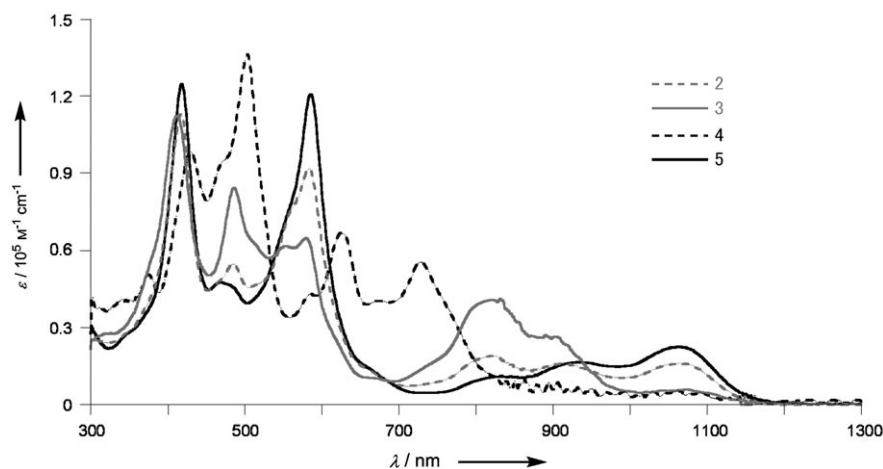


Figure 6. UV/Vis absorption spectra of **2**, **3**, **4**, and **5** in CHCl_3 .

of **2** and **5** but with different relative intensities. The only example of a fused bischlorin was reported by Dolphin et al., exhibiting strong absorption bands around $\lambda=500$ and 700 nm.^[22] Thus the $\lambda=400\text{--}550$ and 600–800 nm bands of **4** might be unique to a bischlorin structure. The absorption spectrum of **5** is quite similar to that of **2**, in line with the fact that the structure of **5** contains the same triply linked Zn^{II} diporphyrin framework as that of **2**. Comparison of the absorption spectra of **2** and **5** indicates that the overall spectra are similar to each other but there are several distinct differences in the Q-band-like bands. These results suggest small but not negligible electronic interactions between the triply linked diporphyrin and the fused benzene segment, despite the presence of saturated methylene bridges.

As demonstrated above, the cycloaddition reactions of the triply linked Zn^{II} diporphyrin show the unique feature of site-selectivity at the bay area with formation of anomalous [4+4] cycloadduct **4**. The observed site-selectivity occurs despite the expected large steric congestion there, and thus the thermal [4+4] cycloaddition reaction is rare. As the product **4** can be formed from **3** by means of a 1,3-sigmatropic rearrangement (Scheme 3), we examined the possibility of **3**→**4** thermal conversion. However, **3** was thermally rather stable and did not produce **4** under the various conditions examined by changing solvent, temperature, and reaction time. On the basis of these results, we concluded that the anomalous [4+4] cycloadduct **4** is not a secondary product but an initial product from **2** and *o*-xylylene.

To better understand these characteristic reactivities of **2** toward *o*-xylylene, we examined the molecular orbital calculations of *meso*-phenyl-substituted triply linked Zn^{II} diporphyrin (**D**) as a simpler reference molecule and *o*-xylylene (Figure 7), in which *o*-xylylene is dealt with as a singlet species according to the previous experimental result.^[23,24] The calculations showed that the energy levels of the LUMO and HOMO are -2.94 and -4.57 eV for **D**, and -1.84 and -5.15 eV for *o*-xylylene, respectively. Therefore, the energy gaps between the LUMO and HOMO are calculated to be 2.73 and 2.21 eV for the interactions between LUMO(*o*-xylylene) versus HOMO(**D**) and between LUMO(**D**) versus HOMO(*o*-xylylene), respectively. A large and distinct difference in the energy gap strongly suggests that the cycloadditions are mainly controlled by the interactions between LUMO(**D**) and HOMO(*o*-xylylene) which has a smaller

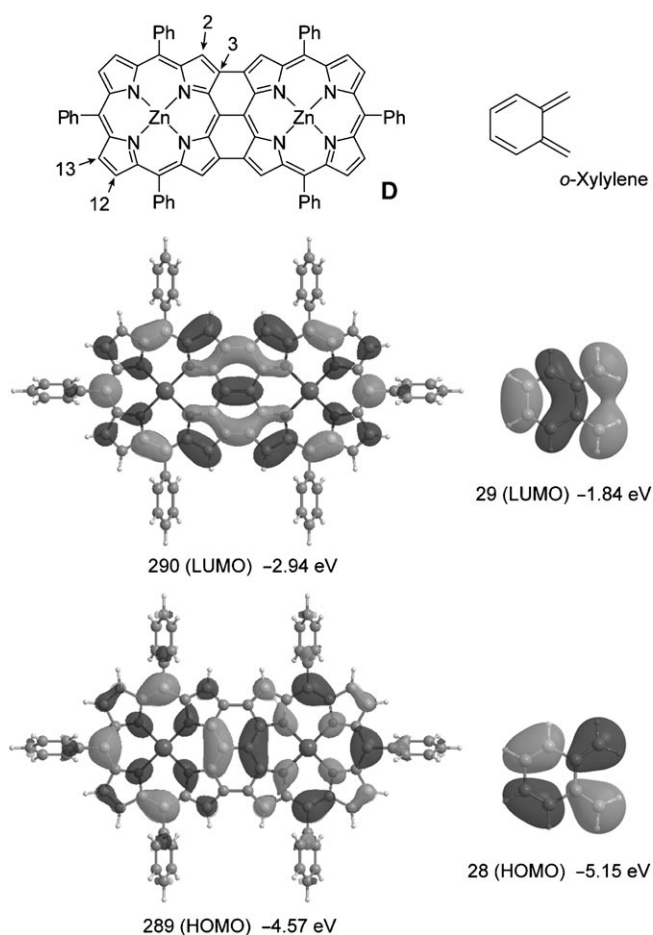
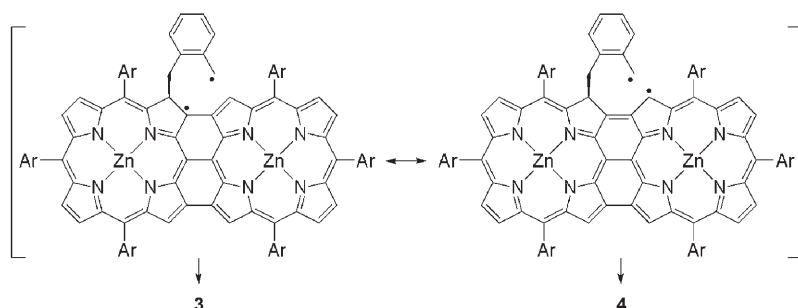


Figure 7. Frontier molecular orbitals of *meso*-phenyl-substituted triply linked Zn^{II} diporphyrin (**D**) and *o*-xylylene.

energy gap. Then, the observed site-selectivity for the formation of **3** can be understood in terms of favorable interactions between LUMO(**D**) and HOMO(*o*-xylylene), in that the large MO coefficients of LUMO(**D**) at C² and C³ positions match nicely with HOMO(*o*-xylylene) (see Supporting Information).

On the other hand, the formation of the [4+4] cycloadduct **4** is rare and difficult to explain, as such [4+4] cycloadditions are usually thermally forbidden and require help in symmetry-breaking, such as photochemical activation or by the use of a transition-metal catalyst. Accordingly, only a few examples of thermal [4+4] cycloaddition reactions are known.^[25,26] One interesting example is the dimerization of 2,3-dimethylene-2,3-dihydrofurans generated by flash vacuum pyrolysis.^[25a,b] The mechanism of the reaction was postulated to be stepwise, involving a biradical intermediate to afford the [4+4] product with *exo* se-



Scheme 3. Proposed reaction mechanism via a diradical intermediate.

lectively. Another interesting example is the [4+4] cycloaddition reaction of *meso*-tris(pentafluorophenyl)-substituted corrole and pentacene along with normal [4+2] Diels–Alder products.^[26] No mechanistic discussion was given in the literature but the corrole system has been shown to become a radical species upon metallation^[27] or incorporation of a COT core segment.^[11d] Thus, the formation of **4** may be rationalized in terms of a similar stepwise radical mechanism. As the C²-position of **D** exhibits the largest MO coefficients among the β -positions, the addition of *o*-xylylene as a 1,4-biradicaloid species at this site may form a 1,4-biradical, the ring-closure of which will produce **4** (Scheme 3). Such an anomalous reactivity may be ascribed to highly conjugated and thus electronically quite polarizable properties of triply linked diporphyrins.

Conclusion

The cycloaddition reactions of the triply linked Zn^{II} diporphyrin **2** with *o*-xylylene have been demonstrated as the first example of the chemical fabrication of triply linked diporphyrins. The two products, the porphyrin–chlorin hybrid dimer **3** and symmetric chlorin dimer **4** were isolated and characterized as [4+2] and [4+4] cycloadducts at the bay-area of **2**. These site-selectivities can be explained by the orbital characteristics of **2**. The cycloadduct **4** was oxidized to **5**. The structures of **3** and **5** have been determined by single-crystal X-ray diffraction analyses. Further studies on the detailed mechanism of the cycloaddition reaction and the exploration of other cycloaddition reactions of triply linked diporphyrins are on going in our laboratory.

Experimental Section

General procedures: 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 in ppm relative to CHCl₃ (δ = 7.26 ppm) or C₆H₆ (δ = 7.16 ppm). Mass spectra were recorded on a Shimadzu/KRATOS KOMPACT MALDI 4 spectrometer by using the positive-MALDI ionization method with/without 9-nitroanthracene or dithranol matrix or on a BRUCKER microTOF in positive-ion mode and with CH₃CN as a solvent. The spectroscopic grade CHCl₃ was used as a solvent for all spectroscopic studies. UV/Vis absorption was recorded on a Shimadzu UV-3100 spectrometer and a Shimadzu RF-5300PC, respectively. Preparative separations were performed by silica-gel flash column chromatography (Merck Kiesegel 60H Art. 7736) and silica-gel gravity column chromatography (Wako gel C-400).

Computational calculations: All calculations were carried out by using the Gaussian 03 program.^[28] All structures were optimized with Becke's three-parameter hybrid exchange functional and the Lee–Yang–Parr correlation functional (B3LYP) without symmetry restriction,^[29] employing the LANL2DZ basis set for the zinc atom and the 6-31G* basis set for the other atoms.

Reaction of triply linked porphyrin dimer **2 and benzosultine:** A solution of benzosultine in toluene (0.2 M, 0.14 mL) was added every 15 min to a stirred solution of **2** (100 mg, 0.054 mmol) in toluene (10 mL) at reflux under a nitrogen atmosphere in the dark. After adding a total of 7 equiv,

the solution was stirred for 30 min at reflux. After this time, the reaction mixture was cooled down to room temperature and the solvent was removed under the reduced pressure. The residue was separated by silica-gel column chromatography to give recovered **2** as a first purple fraction, **3** as a pinkish purple fraction, and **4** as a green fraction. They were purified by recrystallization from CH₂Cl₂/CH₃CN. Yield: 22.4 mg, 0.011 mmol, 21% (**3**) and 16.1 mg, 0.0082 mmol, 15% (**4**).

Compound 3: ¹H NMR (C₆D₆): δ = 9.15 (s, 1H; H^l), 8.95 (s, 1H; H^k), 8.87 (d, J = 4.6 Hz, 1H; Chl- β), 8.82 (d, J = 4.6 Hz, 1H; Chl- β), 8.78 (d, J = 4.6 Hz, 1H; Chl- β), 8.73 (d, J = 4.6 Hz, 1H; Chl- β), 8.45 (s, 1H; Ar), 8.43 (s, 1H; Ar), 8.38 (d, J = 4.3 Hz, 1H; Por- β), 8.35 (s, 1H; Ar), 8.33 (m, 1H; Ar), 8.28 (s, 1H; Ar), 8.27 (d, J = 4.4 Hz, 1H; Por- β), 8.19 (s, 1H; Ar), 8.14 (s, 1H; Ar), 8.11 (s, 1H; Ar), 8.10 (d, J = 2.7 Hz, 1H; Ar), 8.07 (d, J = 4.6 Hz, 1H; Por- β), 8.01 (s, 2H; Ar), 8.00 (d, J = 3.8 Hz, 1H; Por- β), 7.95 (s, 1H; Ar), 7.92 (m, 1H; Ar), 7.91 (s, 1H; Ar), 7.85 (s, 1H; Ar), 7.81 (s, 1H; Ar), 7.79 (s, 1H; Ar), 7.73 (s, 1H; Ar), 7.71 (s, 1H; H^l), 7.00 (m, 1H; benzo), 6.82 (t, J = 7.4 Hz, 1H; benzo), 6.49 (t, J = 7.2 Hz, 1H; benzo), 6.11 (d, J = 7.3 Hz, 1H; benzo), 5.85 (t, J = 7.1 Hz, 1H; H^c), 3.39 (d, J = 14.9 Hz, 1H; CH₂), 3.34 (dd, J = 15.6, 7.0 Hz, 1H; CH₂), 3.11 (d, J = 14.9 Hz, 1H; CH₂), 2.92 (dd, J = 15.6, 7.0 Hz, 1H; CH₂), 1.59 (s, 9H; *t*Bu), 1.58 (s, 18H; *t*Bu), 1.57 (s, 9H; *t*Bu), 1.56 (s, 9H; *t*Bu), 1.55 (m, 27H; *t*Bu), 1.49 (s, 9H; *t*Bu), 1.47 (s, 9H; *t*Bu), 1.43 (s, 9H; *t*Bu), 1.42 ppm (s, 9H; *t*Bu); HR-ESI-MS: m/z : calcd for C₁₃₂H₁₄₇N₈Zn₂: 1976.0343 [M+H]⁺; found: 1976.0372; UV/Vis (CHCl₃): λ_{\max} (ϵ) = 412 (112000), 486 (84000), 579 (65000), 820 nm (41000 M⁻¹ cm⁻¹).

Compound 4: ¹H NMR (CDCl₃): δ = 9.17 (s, 2H; H^b), 8.40 (d, J = 4.6 Hz, 2H; Chl- β), 8.31 (d, J = 4.1 Hz, 2H; Chl- β), 8.26 (s, 2H; Ar), 8.21 (d, J = 4.6 Hz, 2H; Chl- β), 8.18 (d, J = 4.1 Hz, 2H; Chl- β), 8.12 (s, 2H; Ar), 8.10 (s, 2H; Ar), 8.01 (s, 2H; Ar), 7.97 (s, 2H; Ar), 7.87 (s, 2H; Ar), 7.82 (s, 2H; Ar), 7.79 (s, 2H; Ar), 7.68 (s, 2H; Ar), 6.95 (dd, J = 5.7 Hz, 2H; benzo), 6.17 (d, J = 9.2 Hz, 2H; H^c, H^c), 5.83 (dd, J = 5.3 Hz, 2H; benzo), 3.88 (d, J = 13.8 Hz, 2H; H^b, H^b), 3.28 (dd, J = 13.8, 9.2 Hz, 2H; H^a, H^a), 1.66 (s, 18H; *t*Bu), 1.57 (s, 18H; *t*Bu), 1.56 (s, 18H; *t*Bu), 1.52 (s, 18H; *t*Bu), 1.44 (s, 18H; *t*Bu), 1.35 ppm (s, 18H; *t*Bu); HR-ESI-MS: m/z : calcd for C₁₃₂H₁₄₆N₈Zn₂: 1975.0254 [M]⁺; found: 1975.0168; UV/Vis (CHCl₃): λ_{\max} (ϵ) = 429 (98000), 503 (136000), 625 (67000), 729 nm (56000 M⁻¹ cm⁻¹).

Compound 5: DDQ (3.0 mg, 0.013 mmol) was added to a solution of **4** (10.1 mg, 0.0051 mmol) in CHCl₃ (10 mL) bubbled with nitrogen in advance. The resulting mixture was stirred for 1 h at room temperature under a nitrogen atmosphere in the dark. After this time, the reaction mixture was passed through an alumina column with THF as an eluent. The solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography and then recrystallized from CH₂Cl₂/CH₃CN. Yield: 8.7 mg, 0.0044 mmol, 86%; ¹H NMR (CDCl₃, at -60 °C): δ = 7.98 (s, 2H; Ar), 7.84 (d, J = 4.6 Hz, 2H; Por- β), 7.82 (d, J = 4.6 Hz, 2H; Por- β), 7.77 (d, J = 4.6 Hz, 2H; Por- β), 7.69 (d, J = 4.6 Hz, 2H; Por- β), 7.66 (s, 2H; Ar), 7.64 (s, 2H; Ar), 7.61–7.60 (m, 4H; Ar), 7.57–7.56 (m, 4H; Ar), 7.54 (s, 2H; Ar), 7.47 (s, 2H; Ar), 7.39 (s, 2H; H^e), 6.99 (dd, J = 5.9 Hz, 2H; benzo), 6.82 (dd, J = 5.5 Hz, 2H; benzo), 4.18 (d, J = 15.6 Hz, 2H; CH₂), 2.98 (d, J = 15.6 Hz, 2H; CH₂), 1.68 (s, 18H; *t*Bu), 1.46 (s, 18H; *t*Bu), 1.42 (s, 18H; *t*Bu), 1.40 (s, 18H; *t*Bu), 1.38 (s, 18H; *t*Bu), 1.36 ppm (s, 18H; *t*Bu); HR-ESI-MS: m/z : calcd for C₁₃₂H₁₄₄N₈Zn₂: 1973.0097 [M]⁺; found: 1973.0148; UV/Vis (CHCl₃): λ_{\max} (ϵ) = 418 (139000), 469 (53000), 586 (135000), 1063 nm (25000 M⁻¹ cm⁻¹).

Preparation of triply linked Ni^{II} diporphyrin: TFA (1.0 mL) was added to a stirred solution of **2** (100 mg, 0.054 mmol) in CHCl₃ (100 mL) at room temperature under a nitrogen atmosphere in the dark and the resulting solution was stirred for 1 h. After this time, the solution was poured into water and the product was extracted with CH₂Cl₂. Recrystallization from a mixture of CH₂Cl₂ and acetonitrile provided triply linked free-base diporphyrin (41.5 mg, 0.024 mmol, 44%), which was then metallated by treatment with Ni(acac)₂ (30 mg, 0.12 mmol) in toluene (10 mL) under reflux for 3 h. After the same work up as above, recrystallization from a mixture of CH₂Cl₂ and acetonitrile gave triply linked Ni^{II} diporphyrin (44.0 mg, 0.024 mmol, 99%). Conversions from **3** and **5** to the corresponding Ni complexes were performed by following a similar method.

Crystallographic data: X-ray data were taken on a BRUKER-APEX X-ray diffractometer equipped with a large area CCD detector. The structures were solved by direct methods (Sir 97^[30] or SHELXS-97^[31a]) and refined by the full-matrix least square technique (SHELXL-97).^[31a] In the event of the solvent molecules not being adequately modeled, the core porphyrin molecules were refined without the solvent molecules by a combination of the SHELX-97 and PLATON SQUEEZE programs.^[31b] CCDC-659310 (2), -659212 (3), and -658838 (5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre www.ccdc.cam.ac.uk/data_request/cif.

Crystallographic data for 2: C₁₃₀H₁₃₈N₈O₂Zn₂; M_w = 1969.22; triclinic; P $\bar{1}$ (no. 2); a = 9.470(5), b = 17.777(5), c = 20.949(5) Å; α = 78.192(5), β = 80.508(5), γ = 80.420(5)°; V = 3373(2) Å³; ρ_{calcd} = 0.973 g cm⁻³; Z = 1; R₁ = 0.0867 (I > 2.0 σ (I)), wR₂ = 0.2514 (all data); GOF = 0.955 (I > 2.0 σ (I)). Crystals were grown from toluene/2-propanol.

Crystallographic data for 3: Empirical formula: C₁₃₈H₁₄₆N₈O₂Zn₂; M_w = 2055.35; triclinic; P $\bar{1}$ (no. 1); a = 14.239(4), b = 14.401(4), c = 18.011(4) Å; α = 99.521(3), β = 91.276(4), γ = 95.009(4)°; V = 3625.9(15) Å³, ρ_{calcd} = 1.050 g cm⁻³; Z = 1; R₁ = 0.0960 (I > 2.0 σ (I)), wR₂ = 0.2643 (all data); GOF = 0.924 (I > 2.0 σ (I)). Crystals were grown from chloroform/ethanol.

Crystallographic data for 5: Empirical formula: C₁₄₀H₁₄₈Cl₂N₈O₂Zn₂; M_w = 2176.30; monoclinic; Cc (no. 9); a = 21.179(3), b = 19.574(3), c = 37.531(6) Å; β = 95.462(5)°; V = 15488(4) Å³; ρ_{calcd} = 0.933 g cm⁻³; Z = 4; R₁ = 0.0957 (I > 2.0 σ (I)), wR₂ = 0.2750 (all data); GOF = 0.949 (I > 2.0 σ (I)). Crystals were grown from 1,2-dichloroethane/2-propanol.

Acknowledgements

This work was partly supported by a grant-in-aid for scientific research from the Ministry of Education, Culture, Sports, Science, and Technology (Japan; no. 19205006). Y.N. acknowledges the Research Fellowships of the JSPS for Young Scientists. We thank Dr. K. Yoza of Bruker AXS for his help in refinement of the crystal structures.

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Received: September 5, 2007
Published online: November 12, 2007