Expanded Porphyrins

Anthracene-Bridged Z-Shaped [26]Hexaphyrin(1.1.1.1.1.1.1.1) Dimer from the Regioselective Diels–Alder Reaction of a Hexaphyrin with Bis-*o*-xylylene Equivalents

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Expanded porphyrins which are porphyrin analogues with more than five pyrrolic subunits have recently attracted much attention because of their interesting structural and functional features and unique metal-coordination properties.[1] However, until now, there have been only a few reports on the chemical transformation of expanded porphyrins.[2] Herein, we report the Diels–Alder reaction of [26]hexaphyrin **1** with *o*-xylylene as the first example of a concerted cycloaddition of *meso*-aryl-substituted expanded porphyrins. Porphyrin (**P**) has an 18-π-aromatic electronic system and the peripheral diagonal double bonds are partially isolated from this aromatic conjugation. This situation explains the reactivity of the peripheral double bonds of **P** in cycloaddition reactions.[3] In this regard, [26]hexaphyrin(1.1.1.1.1.1) (**H**)[4] may also potentially undergo related cycloaddition reactions because the diagonal and inverted pyrrolic double bonds do not participate in the aromatic circuit.

A solution of hexakis(pentafluorophenyl)-substituted [26]hexaphyrin(1.1.1.1.1.1) **1** (5 mM) and benzosultine **3**[5] (1.3 equiv) in benzene was heated at reflux for 24 h under nitrogen atmosphere. After cooling the reaction mixture to room temperature, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 5 equiv) was added, and the resulting mixture was stirred for a further 12 h. Separation by column chromatography through silica gel provided naphthohexaphyrin **4** (55%) and bisnaphthohexaphyrin **5** (4.6%). FAB mass spectrometry revealed a molecular weight of 1560 for **4** which indicates the addition of one *o*-xylylene unit to **1**. The ^{1}H NMR spectrum of **4** exhibited a symmetric feature involving four doublets at $\delta = 9.12$, 9.07, 8.88, and 8.84 ppm (all $J = 4.6$ Hz) owing to the outer β-pyrrolic protons, a singlet at $\delta = -0.07$ ppm for the inner NH protons, and a singlet at $\delta = -2.50$ ppm for the inner β-pyrrolic protons. Characteristically, the protons of the fused naphthalene ring appeared at $\delta = 5.55$ (H^3), 3.53 (H^2), and 1.31 ppm (H^1). The observed

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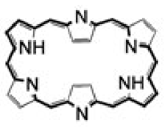

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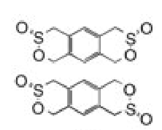

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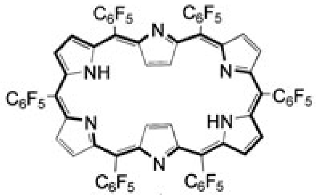

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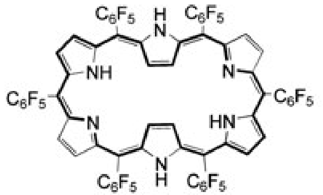

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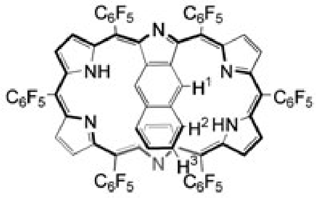

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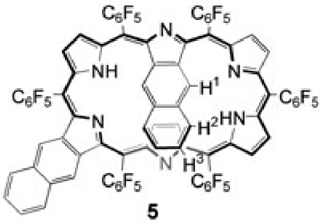

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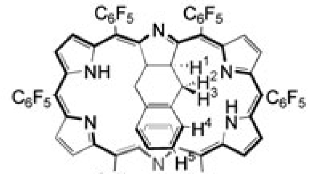

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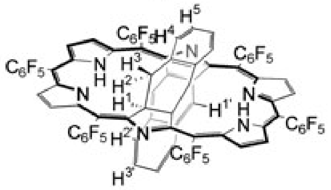

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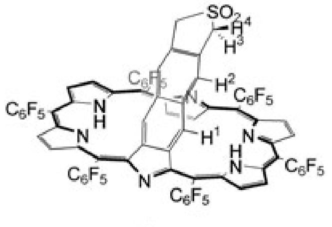

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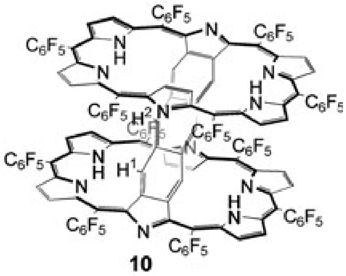

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substantial highfield shifts can be ascribed to the diamagnetic ring current of [26]hexaphyrin and a bent orientation of the fused naphthalene ring with respect to the hexaphyrin plane. These data correspond with the structure of **4**, which results from the Diels–Alder reaction at the inner β-pyrrolic double bond in **1**. The strong ring current as suggested from these data indicates that the aromatic character is preserved in **4**. The ESI mass spectrum of **5** showed a peak for its parent ion at $m/z = 1661$, which indicates the addition of two *o*-xylylene units to **1**. The ^{1}H NMR spectrum of **5** showed two different sets of signals for the protons on the fused naphthalene rings, and as these were observed at high and low fields, the adduct **5** is assigned to have both inner and outer fused naphthalene rings.[6] When the reaction was stopped before the oxidation with DDQ, the initial adduct **6** was isolated in 43% yield along with the recovery of **1** (28%) and reduced [28]hexaphyrin **2** (10%). Oxidation of **6** with DDQ gave **4** quantitatively. The ^{1}H NMR spectrum of **6** exhibits peaks at $\delta = -6.07$ (H^1), -5.10 (H^2), -3.79 (H^3), 4.06 (H^4), and 5.64 ppm (H^5) owing to the protons in the fused tetrahydronaphthalene moiety. The structure of **6** was confirmed further by X-ray crystallographic analysis (Figure 1).[7]

We carried out theoretical calculations at the B3LYP/6–31G* level on hexaphyrin **1** and **6′**, a cycloadduct between **1** and 1,3-butadiene. Figure 2 illustrates the LUMOs for **1** and **6′** and shows clear differences in their distributions. The LUMO of hexaphyrin **1** develops at both the inner and outer double bonds. However, the LUMO of **6′** has very small coefficients at the inverted β-pyrrolic double bond. This result leads to the following predictions: 1) the initial Diels–Alder reaction can occur at either inner or outer double bonds[8] and 2) the second cycloaddition never takes place at the other side of the inner double bond once one of the inner double bonds has reacted with a 1,3-diene. The preferential formation of **4** suggests that the inner inverted β-pyrrolic double bonds are the most reactive and that the second prediction is indeed consistent with the formation of **5**. Interestingly, however, the [26]hexaphyrin aromatic system is restored in the oxidized adduct **4** because the DFT calculation predicts that the LUMO of **4′** develops significantly at the inverted β-pyrrolic double bond, as in **1** (Figure 2). Thus, we examined the reactivity of **4** toward *o*-xylylene and obtained the bis-*o*-xylylene adduct **7** as a major product in 33% yield. The ^{1}H NMR spectrum of **7** exhibits peaks at $\delta = -8.00$ (H^1), -4.06 (H^2), -3.27 (H^3), 2.98 (H^4), and 5.20 ppm (H^5) owing to the protons in the fused tetrahydronaphthalene moiety and at $\delta = 0.95$ (H$^{1'}$), 3.47 (H$^{2'}$), and 5.54 ppm (H$^{3'}$) in the fused naphthalene moiety. Curiously, the adduct **7** could not be oxidized with DDQ even under rather forcing conditions. Importantly, the regioselectivity during the addition of the second *o*-xylylene unit can be controlled by the oxidation state of the initial addition site, probably through electronic communication along the hexaphyrin macrocycle.

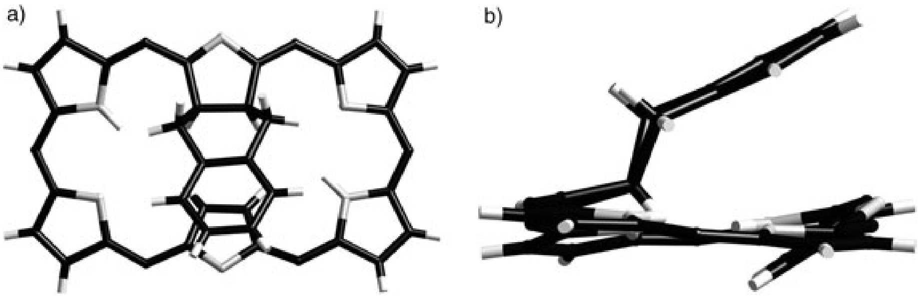

Figure 1. X-ray crystal structure of **6**. a) Top view and b) side view. *meso*-Pentafluorophenyl substituents are omitted for clarity.

It then occurred to us that the use of benzodisultine **8**[9] as a diene toward **1** may lead to the formation of a hexaphyrin dimer in which two hexaphyrin rings are bridged by an anthracene spacer. With this expectation, a solution of **1** (20 mM) and **8** (18 mM) in benzene was heated at 80 °C for 48 h and then subjected to oxidation with DDQ at room

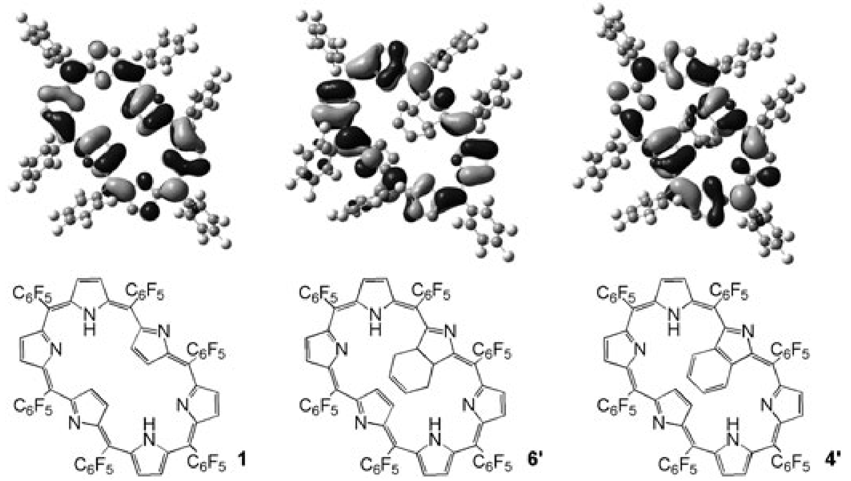

Figure 2. DFT calculations of hexaphyrin **1**, cycloadduct **6′**, and the oxidized adduct **4′**. LUMOs of **1** (left), **6′** (middle), and **4′** (right).

temperature. Two adducts, **9** (24%) and **10** (20%), were isolated along with some unconverted starting material **1** (21%). The FAB mass spectrum of **9** showed a peak for the parent ion at $m/z = 1650$ (calcd for $C_{76}H_{20}F_{30}N_6SO_2$: 1650), and its ^{1}H NMR spectrum exhibited a symmetric structure similar to that of **4** with additional AB-quartet signals at $\delta = 3.17$ and 3.00 ppm (H^3 and H^4) with $J = 15$ Hz. The IR spectrum of **9** showed bands at $\tilde{\nu} = 1333$ and 1135 cm^{-1} which were assigned to transitions in the sulfone functionality. Thermal rearrangement of sultine to sulfone in the initial Diels–Alder adduct can explain the formation of **9**. The naphthosulfolene-fused hexaphyrin structure of **9** was confirmed by X-ray crystallographic analysis (Figure 3).[10] The fused sulfolene–naphthalane moiety is bent toward the hexaphyrin core with a dihedral angle of approximately 43.0°, and this structure explains the highfield shift of the fused naphthosulfolene moiety.

The product **10** displayed its parent-ion peak at $m/z = 3043.1875$ (high resolution ESI-MS: calcd for $C_{142}H_{31}N_{12}F_{60}$: 3043.1831 [$(M+H)^+$]). The ^{1}H NMR spectrum of **10** supports its symmetric zigzag structure with the protons at the anthracene bridge appearing upfield as singlets at $\delta = 0.37$ (4H) and 0.10 ppm (2H). Indeed, the zigzag structure of **10** has been elucidated by X-ray diffraction studies with the fused anthracene unit bridging two hexaphyrin units with a dihedral angle of 42.7° (Figure 4).[11] Obviously, Diels–Alder reactions occurred consecutively at both diene moieties of bis-*o*-xylylene with two hexaphyrin molecules to give rise to the unique Z-shape double-decker structure of **10** with an interplanar distance of the hexaphyrins of 6.34 Å.

Figure 4. X-ray crystal structure of **10**. *meso*-Pentafluorophenyl groups are omitted for clarity.

The absorption spectra of **4, 5**, and **10** are shown along with that of **1** in Figure 5. The Soret-like bands of **4** and **5** are broadened and red-shifted, which probably reflect the perturbations imposed by the fused naphthalene. On the other hand, the absorption spectrum of **10** exhibits a blue-shifted Soret-like band at $\lambda_{max} = 545$ nm with a full width at half maximum (fwhm) of 3220 cm^{-1}, which is rather broad relative to that for **1** (1590 cm^{-1}). These observations may be accounted for in terms of exciton coupling between the two hexaphyrin chromophores arranged in a face-to-face fashion[12] and hence suggest that **10** is a useful platform to study the excitonic interaction between aromatic [26]hexaphyrins.

In summary, the Diels–Alder reaction of **1** with *o*-xylylene occurs selectively at the inner C−C double bond to provide novel aromatic ring-fused hexaphyrins. Furthermore, the use of benzodisultine as a bis-*o*-xylylene equivalent furnished the anthracene-bridged double-decker hexaphyrin **10**. This is the first example of a concerted cycloaddition reaction that involves the peripheral double bond of *meso*-aryl-substituted expanded porphyrins. Explorations of cycloaddition reactions of other expanded porphyrins with 1,3-dienes or 1,3-dipolarophiles are ongoing in our laboratory.

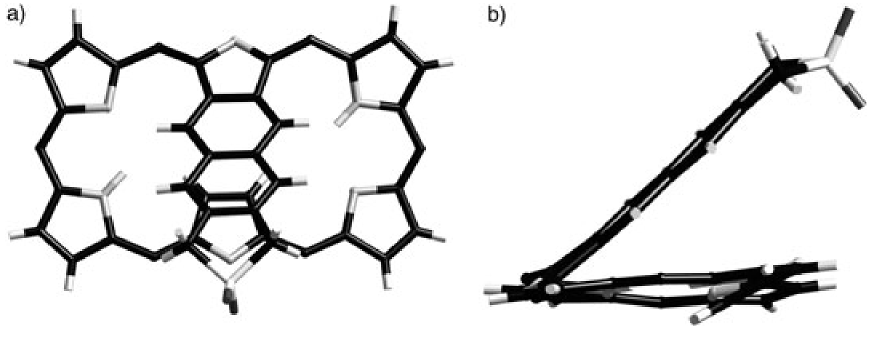

Figure 3. X-ray crystal structure of **9**. a) Top view and b) side view. *meso*-Pentafluorophenyl substituents are omitted for clarity.

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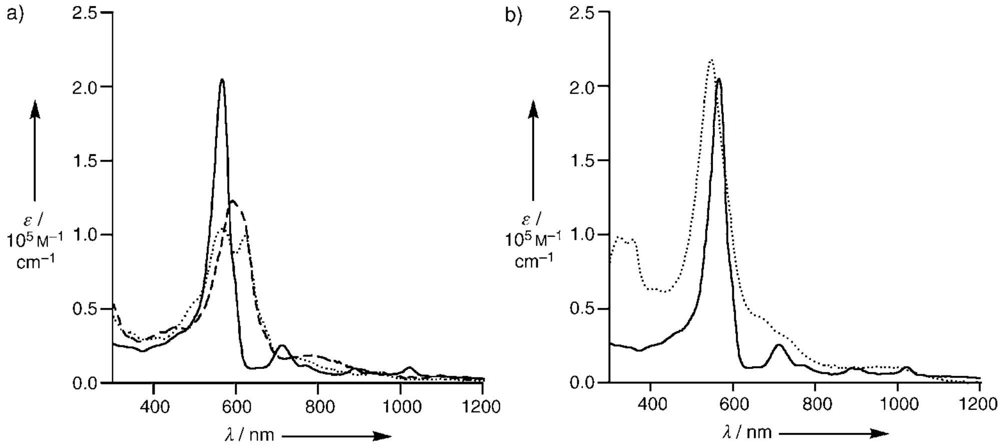

Figure 5. UV/Vis spectra of a) **1** (——), **4** (•••••), and **5** (– – –), and b) **1** (——) and **10** (•••••).

Keywords: cycloaddition · diene ligands · heterocycles · macrocycles · porphyrinoids

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[6] We could not determine the exact structure of compound **5**. The position at which the outer naphthalene ring is fused to the hexaphyrin core is still ambiguous.

[7] Crystal data for **6** ($C_{74}H_{22}F_{30}N_6$): $M_W = 1564.98$, monoclinic $P2_1/n$ (No. 14), $a = 19.68(3)$, $b = 13.79(2)$, $c = 26.23(3)$ Å, $\beta = 95.76(4)°$, $V = 7081(13)$ Å^3, $T = 123$ K, $\rho_{calcd} = 1.468$ g cm^{-3}, $Z = 4$. 61481 reflections were measured, and $R = 0.096$, w$R = 0.124$ for 17777 reflections with $[I > 3\sigma(I)]$, $GOF = 1.399$. CCDC-248442 (**6**), CCDC-248443 (**9**), and CCDC-248444 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[8] The preference for the inner double bond in the initial addition step may be explained in terms of the steric factor of the outer pentafluorophenyl groups.

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[10] Crystal data for **9** ($C_{78}H_{22}F_{30}N_6Cl_4SO_2$): $M_W = 1818.89$, triclinic $P\bar{1}$ (No. 2), $a = 15.582(8)$, $b = 15.939(7)$, $c = 16.93(1)$ Å, $\alpha = 79.58(4)$, $\beta = 64.89(4)$, $\gamma = 66.46(4)°$, $V = 3489(3)$ Å^3, $T = 123$ K, $\rho_{calcd} = 1.731$ g cm^{-3}, $Z = 2$. 64912 reflections were measured, and $R = 0.085$, w$R = 0.136$ for 8104 reflections with $[I > 3\sigma(I)]$, $GOF = 1.272$.

[11] Crystal data for **10** ($C_{158}H_{30}N_{12}F_{60}O_{10}$): $M_W = 3395.95$, triclinic $P\bar{1}$ (No. 2), $a = 10.278(6)$, $b = 18.118(9)$, $c = 18.80(1)$ Å, $\alpha = 97.95(5)$, $\beta = 94.19(5)$, $\gamma = 93.79(4)°$, $V = 3447(3)$ Å^3, $T = 123$ K, $\rho_{calcd} = 1.636$ g cm^{-3}, $Z = 1$. 31007 reflections were measured, and $R = 0.084$, w$R = 0.097$ for 3567 reflections with $[I > 3\sigma(I)]$, GOF = 1.186.

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