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Notes

Synthesis, Structure, and Modeling of a Cyclic Rhodium(III) Porphyrin Dimer with an Encapsulated 4,4′-Bipyridine Ligand

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Introduction

As part of an ongoing project in our laboratory we have prepared cyclic Zn,[1] Ru,[2] Ni,[3] and Sn[4] porphyrin oligomers in which the porphyrin units are linked by acetylenic bridges. These host molecules have been shown to bind a range of substrates, influence the rates and outcomes of Diels−Alder[5,6] reactions, and display catalytic activity toward an acyl transfer[7] reaction.

Rhodium porphyrins have aroused interest on account of their ability to effect catalysis of certain classes of organic reactions such as cyclopropanation,[8−14] enolization,[15] CH activation,[16−22] olefin oxygenation,[23] and borohydride reduction,[24,25] while the axial coordination of amines to Rh porphyrins has been utilized in molecular receptors for amino acids[26−28] and nucleotides.[29,30] Covalently linked dimeric Rh porphyrins have been reported previously with[31] and without[19] metal−metal bonding between the Rh centers.

We report here the synthesis, spectroscopy, and X-ray structure of a butadiyne-linked Rh(III) porphyrin dimer containing a coordinated 4,4′-bipyridine guest. This is compared with the structures of complexes of an analogous monomeric Rh(III) porphyrin with bipyridine and pyridine, and with the results of molecular modeling.

Experimental Section

All chemicals were purchased of reagent grade or better. Merck silica gel 60 was used for column chromatography. NMR spectra were recorded on Bruker instruments operating at 400 or 250 MHz for ^{1}H and 62.9 or 100.6 MHz for ^{13}C. UV−visible spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Mass spectra were recorded on Kratos spectrometers.

5,15-Di(3-trimethylsilylethynylphenyl)-2,8,12,18-tetrahexyl-3,7,-13,17-tetramethylporphyrin (1). This compound was prepared using a variant of straightforward published procedures.[32,33] Purple crystals. Yield: 57%. ^{1}H NMR (CDCl$_3$, 250 MHz): δ 10.23 (s, 2H, meso), 8.18 (m, 2H, Ar), 8.04 (m, 2H, Ar), 7.90 (d, $J = 8$ Hz, 2H, Ar), 7.68 (t, $J = 8$ Hz, 2H, Ar), 3.97 (t, $J = 8$ Hz, 8H, hexyl ^{1}CH$_2$), 2.51 (s, 12H, CH$_3$), 2.17 (m, 8H, hexyl ^{2}CH$_2$), 1.73 (m, 8H, hexyl ^{3}CH$_2$), 1.49 (m, 8H, hexyl ^{4}CH$_2$), 1.37 (m, 8H, hexyl ^{5}CH$_2$), 0.90 (t, $J = 7$ Hz, 12H, hexyl ^{6}CH$_3$), 0.26 (s, 18H, Si(CH$_3$)), −2.46 (s, br, 2H, NH). ^{13}C NMR (62.9 MHz, CDCl$_3$): δ 144.9, 143.4, 142.4, 141.5, 136.1, 136.0, 133.0, 131.8, 127.5, 122.6, 116.7, 105.1, 97.1, 94.5, 33.3, 32.0, 30.0, 26.7, 22.7, 15.0, 14.0, −0.04. UV/vis (CH$_2$Cl$_2$): $\lambda_{\max}$ 408, 506, 542, 576, 626 nm. FAB-MS: m/z 1048.3 (M$^+$).

5,15-(3-Ethynylphenyl)-2,8,12,18-tetrahexyl-3,7,13,17-tetramethylporphyrin (2). To a solution of **1** (973 mg, 0.928 mmol) in CH$_2$Cl$_2$ (100 mL) was added a solution of tetrabutylammonium fluoride (3.0 mL, 1.0 M in THF). Two spatulas of CaCl$_2$ were added to quench the reaction after 30 min. The reaction mixture was washed with water (200 mL × 2), the organic layer dried over magnesium sulfate, the solvent removed under reduced pressure and the product recrystallized from CHCl$_3$/methanol. Yield: 94%. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 10.23 (s, 2H, meso), 8.23 (d, $J = 1$ Hz, 2H, Ar), 8.06 (d, $J = 8$ Hz,

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Table 1. Crystallographic Data of 4, 7 and 8

	4	**7**	**8**
empirical formula	$C_{140}H_{158}Cl_6I_2N_{10}Rh_2$	$C_{132}H_{164}Cl_4I_2N_{10}Rh_2$	$C_{65}H_{81}IN_5Rh$
fw	2653.08	2492.15	1162.16
crystal dimens (mm)	0.10 × 0.06 × 0.02	0.30 × 0.25 × 0.20	0.25 × 0.20 × 0.15
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	15.043(2)	15.207(2)	15.280(2)
b, Å	16.146(2)	17.479(2)	16.062(2)
c, Å	16.596(2)	12.347(2)	12.583(2)
α, deg	63.730(10)	110.27(2)	108.480(10)
β, deg	69.640(10)	90.74(2)	93.770(10)
γ, deg	63.230(10)	95.93(2)	99.220(10)
V, Å^3	3171.1(7)	3058.0(7)	2868.6(7)
Z	1	1	2
$\rho_{\text{calc, Mg/m}^3}$	1.389	1.353	1.345
R	0.0934	0.0476	0.0410
wR2	0.2086	0.1179	0.0927
Goodness of fit on F^2	1.184	1.102	1.045

2H, Ar), 7.93 (d, $J = 8$ Hz, 2H, Ar), 7.71 (t, $J = 8$ Hz, 2H, Ar), 3.97 (t, $J = 8$ Hz, 8H, hexyl $^1CH_2$), 3.17 (s, 2H, C≡CH), 2.50 (s, 12H, CH_3), 2.17 (m, 8H, hexyl $^2CH_2$), 1.72 (m, 8H, hexyl $^3CH_2$), 1.48 (m, 8H, hexyl $^4CH_2$), 1.36 (m, 8H, hexyl $^5CH_2$), 0.89 (t, $J = 7$ Hz, 12H, hexyl $^6CH_3$), −2.45 (s, br, 2H, NH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 144.9, 143.6, 142.6, 141.6, 136.4, 135.9, 133.4, 132.0, 127.7, 121.5, 116.6, 97.2, 83.7, 33.3, 32.0, 30.0, 26.8, 22.7, 15.0, 14.1. UV/vis (CH_2Cl_2): λ_{max} 408, 506, 540, 580, 626 nm. FAB-MS: m/z 903.6 (M^+).

5,15-(3-Ethynylphenyl)-2,8,12,18-tetrahexyl-3,7,13,17-tetramethylporphyrinatorhodium(III) Iodide (3). Freshly distilled CH_2Cl_2 (40 mL) was cannulated to a mixture of **2** (250 mg, 0.276 mmol) and anhydrous sodium acetate (220 mg, 2.686 mmol) under argon, then to this was slowly added a solution of $[Rh(CO)_2Cl]_2$ (131 mg, 0.337 mmol) in CH_2Cl_2 (freshly distilled, 10 mL). The mixture was stirred for 4 h at room temperature under argon in the dark. After I_2 (206 mg, 0.810 mmol) was added, the mixture was stirred for a further 8 h. The insoluble materials were removed by filtration and the solution washed with saturated KI aqueous solution (100 mL) and water (200 mL × 2) successively. The organic layer was dried over magnesium sulfate and evaporated under reduced pressure. The residue was purified by column chromatography eluting with CH_2Cl_2/*n*-hexane (1/1) containing 1% ethyl acetate. The product was recrystallized from CH_2Cl_2/methanol to give red-orange solids. Yield: 44%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.29 (s, 2H, meso), 8.30 (s, 2H, Ar), 8.14 (m, 2H, Ar), 7.95 (m, 1H, Ar), 7.70 (m, 2H, Ar), 4.05−3.88 (m, 8H, hexyl $^1CH_2$), 3.18 (s, 1H, C≡CH), 3.11 (s, 1H, C≡CH), 2.51 (s, 12H, CH_3), 2.19 (m, 8H, hexyl $^2CH_2$), 1.75 (m, 8H, hexyl $^3CH_2$), 1.50 (m, 8H, hexyl $^4CH_2$), 1.38 (m, 8H, hexyl $^5CH_2$), 0.90 (t, $J = 7$ Hz, 12H, hexyl $^6CH_3$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 144.6, 142.9, 141.0, 138.4, 136.9, 136.5, 133.9, 133.5, 132.1, 127.8, 127.4, 121.9, 121.2, 119.0, 100.1, 83.9, 83.6, 64.1, 33.2, 32.0, 31.4, 30.1, 29.3, 27.0, 22.8, 22.1, 16.0, 14.1. UV/vis (CH_2Cl_2): λ_{max} 404, 518, 548 nm. FAB-MS: m/z 1130.6 (M^+).

Rh Dimer·4,4′-Bipyridine complex (4). To a solution of **3** (67.6 mg, 0.060 mmol) and 4,4′-bipyridine (4.55 mg, 0.030 mmol) in CH_2Cl_2 (freshly distilled, 100 mL), CuCl (113 mg, 1.12 mmol), and tetramethylethylenediamine (0.17 mL, 1.13 mmol) were added. The mixture was stirred at room temperature under dry air. After 2 h the solution was washed with water (300 mL × 3) and the organic layer was dried over magnesium sulfate. The solvent was evaporated under reduced pressure and the residue purified by silica gel column chromatography (CH_2Cl_2/*n*-hexane, 1/1). The product was recrystallized from $CHCl_3$/*n*-hexane to give crystalline materials. Yield: 61%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.12 (s, 4H, meso), 8.58 (d, $J = 7$ Hz, 4H, Ar), 7.67 (m, 8H, Ar), 6.58 (s, 4H, Ar), 4.19 (d, $J = 7$ Hz, 4H, pyr-H_β), 3.93 (m, 4H, $^1CH_2$ of hexyl), 3.68 (m, 4H, hexyl $^1CH_2$), 2.21 (s, 12H, CH_3), 1.99 (m, 8H, hexyl $^2CH_2$), 1.66 (m, 8H, hexyl $^3CH_2$), 1.40 (m, 8H, hexyl $^4CH_2$), 1.31 (m, 8H, hexyl $^5CH_2$), 0.86 (t, 12H, hexyl $^6CH_3$), 0.04 (d, $J = 7$ Hz, 4H, pyr-H_α). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 144.5 143.7, 142.9, 139.1, 138.8, 138.6, 137.9, 133.9, 129.8, 127.4, 120.0, 117.3, 116.8, 98.9, 83.5, 73.6, 33.4, 31.9, 30.1, 26.9, 22.8, 16.0, 14.1. UV/vis (CH_2Cl_2): λ_{max} 318, 340, 420, 534, 564 nm. FAB-MS: m/z 2414.4 (M^+).

5,15-Di(phenyl)-2,8,12,18-tetrahexyl-3,7,13,17-tetramethylporphyrin (5). 5 was prepared in a manner similar to **1** affording purple needles. Yield 70%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.23 (s, 2H meso), 7.57 (d, $J = 7$ Hz, 4H, Ar), 7.81−7.71 (m, 6H, Ar), 3.97 (t, $J = 8$ Hz, 8H, hexyl $^1CH_2$), 2.48 (s, 12H, CH_3), 2.18 (m, 8H, hexyl $^2CH_2$), 1.72 (m, 8H, hexyl $^3CH_2$), 1.48 (m, 8H, hexyl $^4CH_2$), 1.34 (m, 8H, hexyl $^5CH_2$), 0.89 (t, $J = 7$ Hz, 12 H, hexyl $^6CH_3$), −2.40 (s, 2H, NH). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 145.1, 143.3, 142.4, 141.4, 136.2, 133.0, 128.2, 127.6, 117.9, 96.9, 33.3, 32.0, 30.0, 26.8, 22.8, 14.6, 14.1. UV/vis (CH_2Cl_2): λ_{max} 400, 506, 540, 574, 626 nm. FAB-MS: m/z 855.6302 (MH^+).

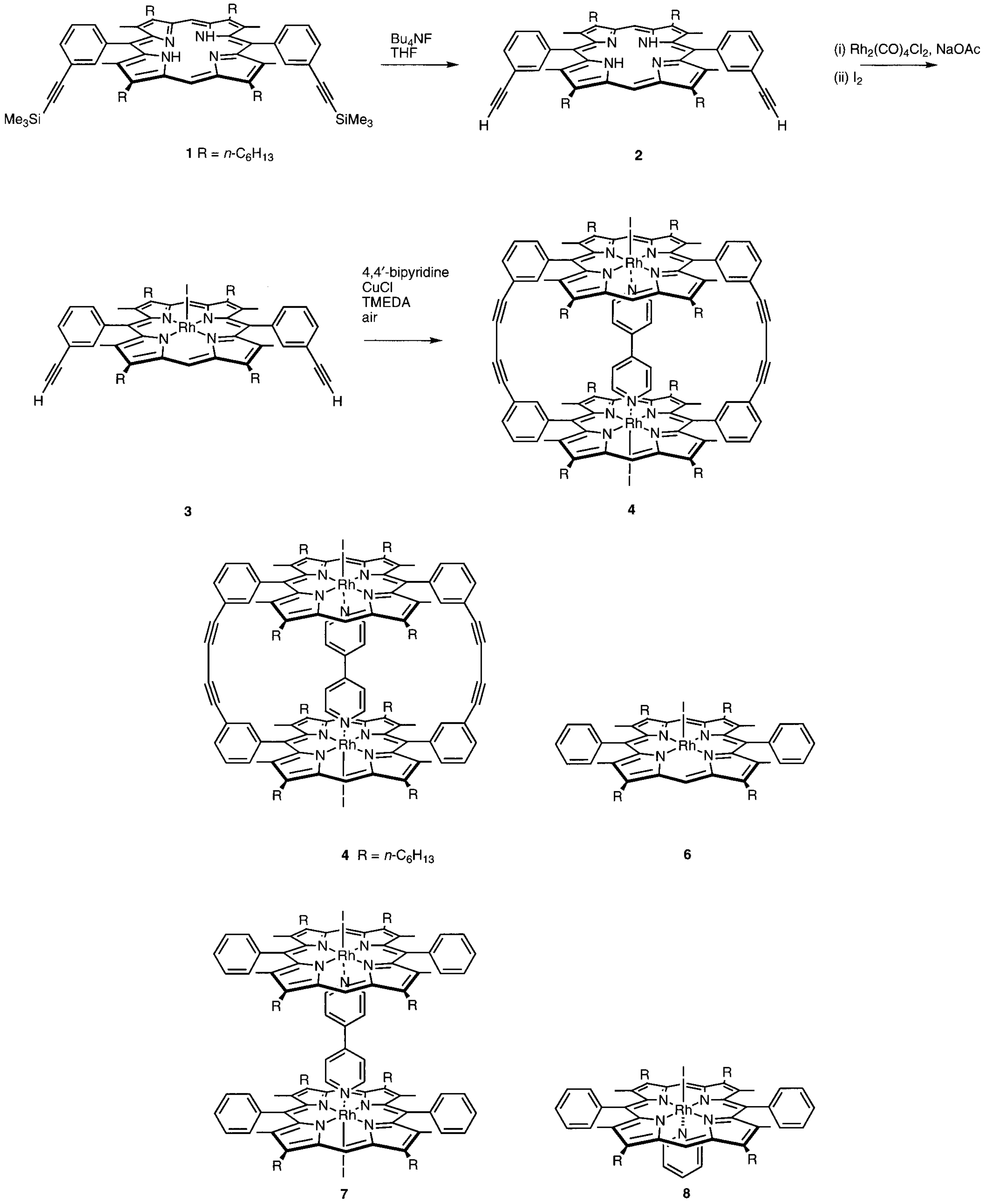
5,15-Di(phenyl)-2,8,12,18-tetrahexyl-3,7,13,17-tetramethylporphyrinatorhodium(III) Iodide (6). Compound **6** was obtained as a deep orange solid and prepared in a manner similar to **3**. Yield 44−89%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.29 (s, 2H, meso), 8.13 (d, $J = 7$ Hz, 2H, Ar), 7.94 (d, $J = 7$ Hz, 2H, Ar), 7.80−7.67 (m, 3H, Ar), 4.04 (m, 4H, hexyl $^1CH_2$), 3.87 (m, 4H, hexyl $^1CH_2$), 2.47 (s, 12H, CH_3), 2.17 (m, 8H, hexyl $^2CH_2$), 1.73 (m, 8H, hexyl $^3CH_2$), 1.48 (m, 8H, hexyl $^4CH_2$), 1.38 (m, 8H, hexyl $^5CH_2$), 0.90 (t, $J = 7$ Hz, 12H, hexyl $^6CH_3$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 144.4, 142.5, 141.5, 141.3, 138.9, 133.2, 133.0, 128.4, 127.7, 127.4, 121.2, 100.7, 33.1, 32.0, 30.0, 26.9, 22.8, 15.5, 14.1. UV/vis (CH_2Cl_2): λ_{max} 402, 548, 522 nm. FIB-MS: m/z 1105.4150 ($M + Na^+$).

6·4,4′-Bipyridine Complex (7). To a stirred solution of 4,4′-bipyridine (50 mg, 0.32 mmol) in THF (0.5 mL) was added **6** (40 mg, 0.037 mmol) in THF (1 mL). After stirring for 3 h at room temperature, the solvent was evaporated and the residue chromatographed on silica eluted with CH_2Cl_2/hexane (1/1) to afford the product as an orange solid. Yield 75%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.97 (s, 4H, meso), 7.70 (m, 8H, Ar), 7.60 (m, 8H, Ar), 4.11 (d, $J = 7$ Hz, 4H, pyr-H_β), 3.76 (m, 16H, hexyl $^1CH_2$), 2.30 (s, 24H, CH_3), 1.99 (m, 16 H, hexyl $^2CH_2$), 1.59 (m, 16 H, hexyl $^3CH_2$), 1.37 (m, 16 H, hexyl $^4CH_2$), 1.25 (m, 16 H, hexyl $^5CH_2$), 0.79 (t, $J = 7$ Hz, 24 H, hexyl $^6CH_3$), 0.39 (d, $J = 7$ Hz, 4H, pyr-H_α). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 144.6, 143.9, 142.6, 140.4, 139.6, 138.4, 133.8, 132.7, 128.2, 127.7, 127.0, 119.1, 117.5, 98.6, 33.2, 31.9, 30.0, 26.9, 22.7, 15.4, 14.1. UV/vis (CH_2Cl_2): λ_{max} 358, 420, 532, 560 nm.

6·Pyridine Complex (8). To a stirred solution of **6** (20 mg, 0.018 mmol) in $CHCl_3$ (1 mL) was added pyridine (50 μL). After several minutes the solvent and excess pyridine were removed under reduced pressure to afford the product as an orange solid in quantitative yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.18 (s, 2H, meso), 8.03 (t, $J = 8$ Hz, 4H, Ar), 7.78 (m, 2H, Ar), 7.70 (m, 4H, Ar), 5.93 (tt, $J = 7, 1$ Hz, 1H, pyr-H_γ), 4.98 (t, $J = 7$ Hz, 2H, pyr-H_β), 3.92 (m, 8H, hexyl $^1CH_2$), 2.45 (s, 12H, CH_3), 2.17 (m, 8H, hexyl $^2CH_2$), 1.71 (m, 8H, hexyl $^3CH_2$), 1.48 (m, 8H, m, hexyl $^4CH_2$), 1.37 (m, 8H, hexyl $^5CH_2$), 0.89 (t, $J = 7$ Hz, 12H, hexyl $^6CH_3$), 0.81 (d, $J = 6$ Hz, 2H, pyr-H_α). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 144.5, 144.0, 143.0, 140.1, 139.8, 138.4, 134.3, 133.9, 133.1, 128.2, 127.7, 127.1, 121.2, 119.2, 98.8, 33.2, 32.0, 30.1, 27.0, 22.8, 15.6, 14.1. UV/vis (CH_2Cl_2): λ_{max} 358, 422, 532, 560 nm.

Reaction of 4 and 7 with MeLi. Methylation of **4** was carried out

Scheme 1



by treatment of a toluene solution of **4** with an excess of MeLi in Et_2O followed by quenching with MeOH and isolation of the product by column chromatography. Methylation of **7** was carried out by a similar procedure except using THF as solvent followed by quenching with EtOAc. Crystals of the product suitable for X-ray analysis were obtained by layering a dichloromethane solution with methanol.

X-ray Crystallography. Crystals of **4** were grown by diffusion of *n*-hexane into a $CHCl_3$ solution. Single crystals of **7** and **8** were obtained by layering solutions in mixed $CHCl_3/CH_2Cl_2$ and toluene respectively with MeOH. Crystal data are given in Table 1.

Diffraction data for **7** and **8** were collected on Rigaku R-Axis IIc imaging plate system. The structures were solved using SHELXS-97[34] and refined with SHELXL-97.[35]

Data for **4** were collected at the Daresbury SRS (UK), Station 9.8, using a Bruker AXS Smart CCD area-detector diffractometer.[36,37] Intensities were integrated[38] from several series of exposures. Each exposure covered 0.6° in ω, with an exposure time of 2 s, and the total data set was more than a hemisphere. Data were corrected for absorption and incident beam decay.[39,40] The unit cell parameters were refined using LSCELL[41] and the structure solved using SIR92[42,43] and refined with SHELXL-97. Even with synchrotron radiation, these crystals were found to be weakly diffracting, resulting in a relatively high R1 value. Extensive disorder is observed in the hexyl chains, typical of this kind of structure.[44] The carbon atoms in these disordered groups were refined with isotropic temperature factors and restrained to give chains with a reasonable geometry.

Molecular Modeling. Molecular modeling was carried out on a Silicon Graphics Indy workstation using CERIUS[2] version 3.0 (BIOSYM/Molecular Simulations) with the UNIVERSAL 1.02 force field.[45] Atom and bond parameters were taken directly from the program database.

Results and Discussion

Cyclic porphyrin dimer **4** containing a bound bipyridine was prepared using a bipyridine templated coupling of two bis-acetylene Rh(III) porphyrins employing the same methodology developed for synthesis of the analogous di-Zn porphyrin dimer (Scheme 1).[1] Mixing solutions of the Rh porphyrin, **6**, and 4,4′-bipyridine at room temperature afforded the ternary complex **7**, while the analogous binary Rh porphyrin-pyridine complex, **8**, was also prepared for comparison.

^{1}H NMR spectroscopy confirmed that the bipyridine ligand remains bound to the porphyrins in solution. The bipyridyl protons are strongly shielded as a result of the porphyrin ring current, with the α and β pyridyl protons of **4** resonating at 0.04 and 4.19 ppm respectively. These resonances were observed at 0.39 and 4.11 ppm in **7** with relative peak intensities consistent with a 2:1 ratio of porphyrin to bipyridine, and are similar to those reported by Thomas[46] and Kadish[47] for dimers of Rh(III) porphyrins bridged by 4,4′-bipyridine and derivatives and to the shielded pyridine resonances observed for **8**.

A number of unsuccessful attempts were made to remove the bipyridine ligand from **4** including refluxing with trifluoroacetic acid in chloroform. Under similar conditions **7** yielded a complex mixture of unidentified products. Despite the lower affinity of Rh(III)-alkyl porphyrins for nitrogen donor ligands,[26,27] displacement of the axial iodo ligands of **4** with MeLi failed to cause dissociation of the bipyridine as judged from the presence of a pair of doublets at 4.40 (H_β) and 1.11 (H_α) ppm in the ^{1}H NMR spectrum of the product.[48] Treatment of **7** with MeLi yielded a product with a single axial methyl group as evidenced by a 3 proton doublet at -6.06 ppm with $J_{Rh-H} = 3$ Hz. However, the resonances from coordinated bipyridine were absent from the spectrum indicating dissociation of the complex. X-ray structure determination confirmed the identity of the product which displayed five coordinate Rh with a Rh−C bond distance of 2.010(5) Å compared to a value of 2.031 Å reported for OEP Rh^{III}Me.[49] The resistance of **4** to dissociation of the bipyridine can be attributed to the preorganization of the cavity for binding of this ligand.[50]

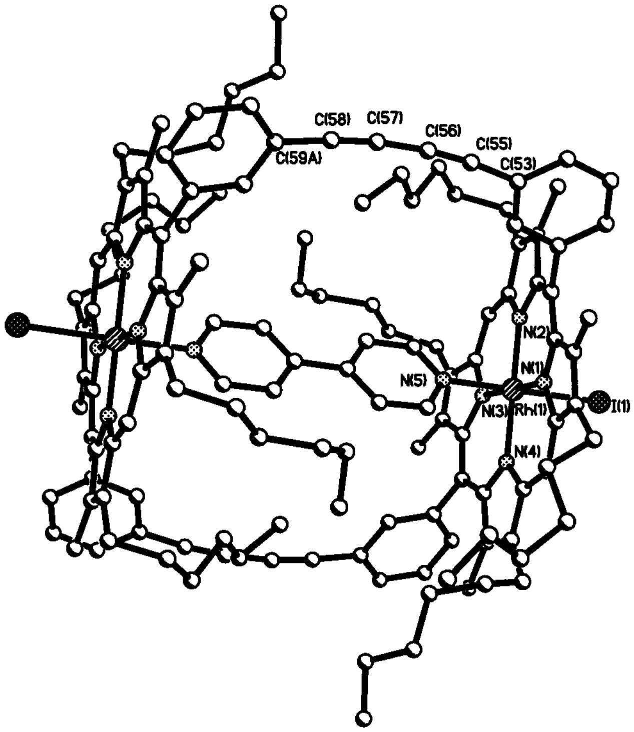


Figure 1. Molecular structure of **4**.

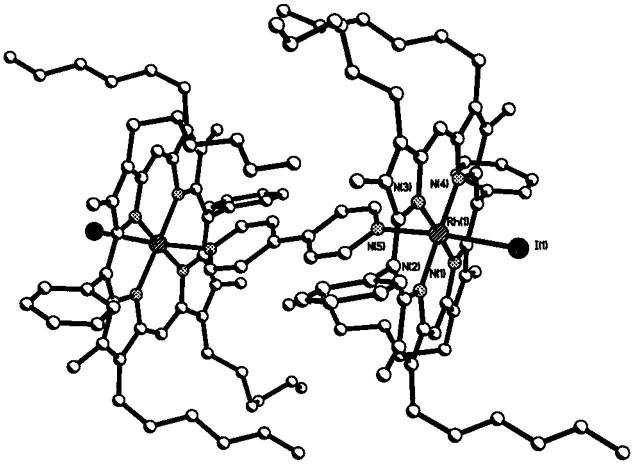


Figure 2. Molecular structure of **7**.

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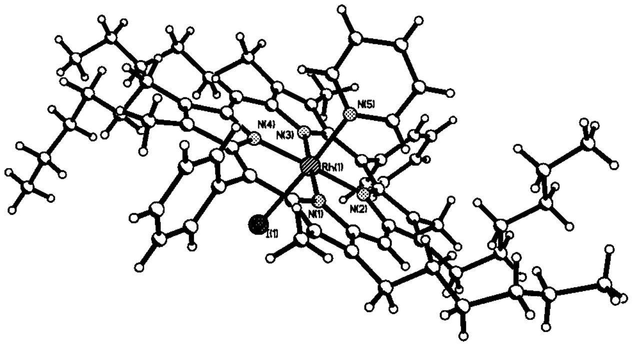

Figure 3. Molecular structure of **8**.

Table 2. Selected Bond Distances (Å) and Angles (deg) of 4, 7, and 8

	4	7	8
Rh1−I1	2.6295(11)	2.6353(8)	2.6305(5)
Rh1−N5	2.100(8)	2.121(4)	2.139(3)
N1−Rh1−N5	89.2(3)	84.27(14)	88.19(12)
N2−Rh1−N5	89.4(3)	89.69(15)	91.99(12)
N3−Rh1−N5	89.2(3)	92.07(15)	90.32(12)
N4−Rh1−N5	90.5(3)	91.64(14)	89.74(12)
N1−Rh1−I1	90.1(2)	90.81(11)	92.48(8)
N2−Rh1−I1	90.9(2)	87.53(11)	91.65(8)
N3−Rh1−I1	91.5(2)	92.88(11)	89.04(8)
N4−Rh1−I1	89.1(2)	91.13(11)	86.62(8)
N5−Rh1−I1	179.2(2)	174.22(10)	176.27(9)
C56−C55−C53	173.5(13)		
C58−C57−C56	173.1(15)		
C55−C56−C57	174.4(15)		
C57−C58−C59A	175.3(14)		

X-ray structure determination of **4**, **7**, and **8** confirmed that the structures proposed in solution on the basis of the NMR spectroscopic evidence persist in the solid state. Views of the molecular structures are given in Figures 1−3 and selected bond distances and angles in Table 2. The dimeric structure of **7** contrasts with the polymeric structure reported for a Mn porphyrin co-crystallized with 4,4′-bipyridine.[51]

Figure 4 shows perpendicular deviations of the atoms of the porphyrins from the best fit plane; the plane calculation did not include the central Rh atom. **7** and **8** exhibit saddle[52] distortions from planarity, whereas for **4** the X-ray structure reveals that the porphyrin moieties are slightly ruffled,[52] the linking aryl groups are bent toward the cavity away from the porphyrin plane and that the butadiyne linkages are slightly bent. The Rh−Rh, Rh−N_{bipy}, and N_{bipy}−N_{bipy} distances are 11.259(2), 2.100(8), and 7.06(2) Å, respectively. The Rh−N distances (Table 2) were essentially unchanged in structures of **4**, **7**, and **8**.

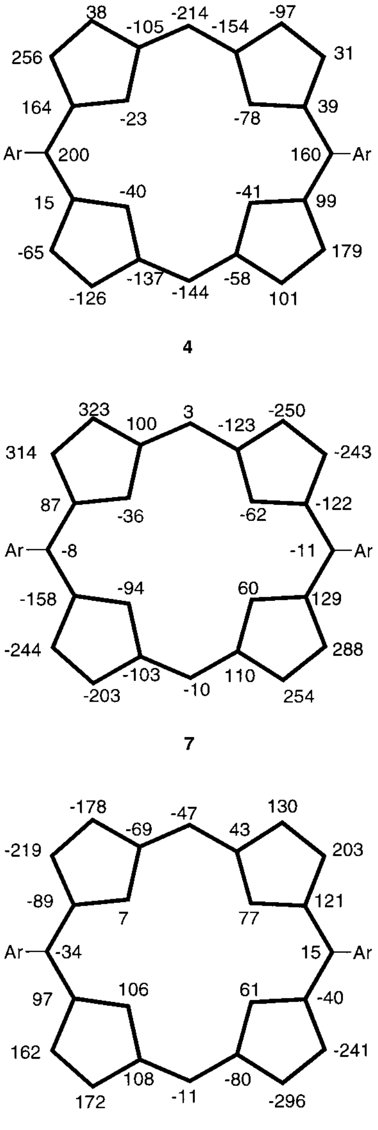

Figure 4. Displacements of the atoms from the best fit porphyrin plane (mÅ). Positive displacement is in the direction of the pyridyl ligand.

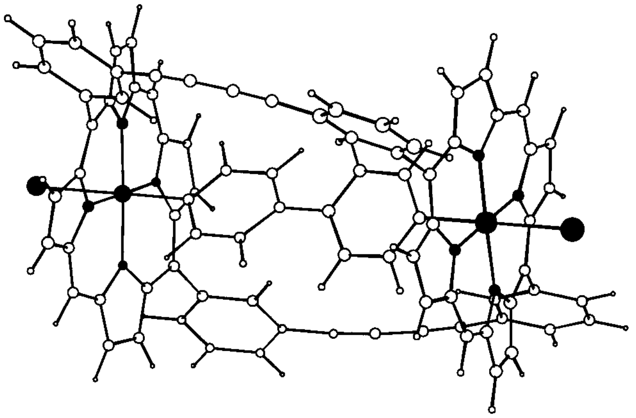

Figure 5. Calculated geometry of **4**.

The geometry obtained for complex **4** (modeled without alkyl substituents) by molecular mechanics calculations (Figure 5) shows a very similar structure to that obtained experimentally (Figure 1), with porphyrin moieties and butadiyne linkages which are ruffled or bent, respectively, and to a similar extent to that in Figure 1. The ruffled distortion is imposed on the porphyrins by the presence of the butadiyne linkers. The calculated Rh−Rh, Rh−N_{bipy}, and N_{bipy}−N_{bipy} distances are 11.2, 2.03, and 7.13 Å.[53] The dihedral angle between the two pyridyl rings in the calculated structure of free bipyridine is 39° and the barrier for rotation around the C4−C4′ bond is calculated to be ~1 kcal/mol. This dihedral angle is smaller (27°) in the calculated geometry of **4** while in the crystal

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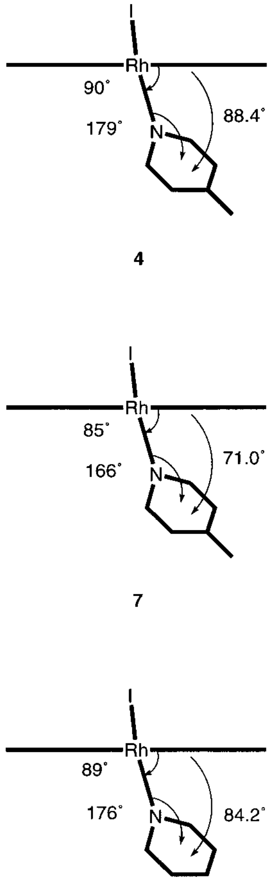

Figure 6. Tilt angles of the Rh−N bond with respect to the pyridine and porphyrin best fit planes, and between the best fit porphyrin and pyridine planes.

structures (Figures 1, 2) the pyridyl rings are almost coplanar. This may result if there is a preferred orientation of the pyridine with respect to the porphyrin, as previously proposed for imidazole ligands;[54,55] the arrangement of the two porphyrin units then inevitably leads to coplanar pyridines. Alternatively an electronic effect in which binding of the porphyrin moieties were to increase conjugation between the two pyridyl rings in bipyridine could be responsible for the observed geometry. A survey of crystal structures of 4,4′-bipyridine bridged metal complexes in the Cambridge database revealed that the eclipsed conformation of the rings is not uncommon.

The angle between the best fit planes of the porphyrin and a single pyridine of **7** is 71.0(1)°. The tilting in **7** arises from a combination of a deviation of the N5−Rh1 bond from the pyridine plane by 14° and of the N5−Rh1 bond from the perpendicular to the porphyrin plane by 5°. This contrasts with the relatively untilted geometry of **8** and **4** for which the angles between the best fit porphyrin and pyridine planes are 84.2(1)° and 88.4(4)° respectively. These angles are illustrated in Figure 6. The calculated structure of **4** also displays an untilted bipyridine. Typically tilted structures have been reported for coordination oligomers of Ru[56] and Zn[57−62] pyridyl porphyrins and the tilts have been ascribed to strain[61] and crystal packing[56] effects.

Summary

We have shown that a covalently linked Rh(III) porphyrin dimer with an encapsulated bipyridine ligand displays a ruffled distortion of the porphyrin units whereas complexes of monomeric Rh porphyrin with bipyridine and pyridine exhibit saddle distortions. The porphyrin distortion in the dimer is induced by the butadiyne linkers which are themselves only slightly distorted. The ligand is highly resistant to dissociation, thereby inhibiting attempts to assess the catalytic potential of the dimer. An analogous complex lacking the linker was found to have a tilted bipyridine ligand in the solid state, which appears to be a characteristic of porphyrin coordination oligomers.

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Supporting Information Available: Thermal ellipsoid plots and crystallographic data, in CIF format, for **4**, **7**, **8**; product of reaction of **7** with MeLi; equations of least squares planes and deviations from them for **4**, **7**, and **8**; cambridge crystallographic database refcodes for structures of 4,4′-bipyridine metal complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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