410 *J. Am. Chem. Soc.* **2000,** *122,* 410−411

Direct Observation of the "Pac-Man" Effect from Dibenzofuran-Bridged Cofacial Bisporphyrins

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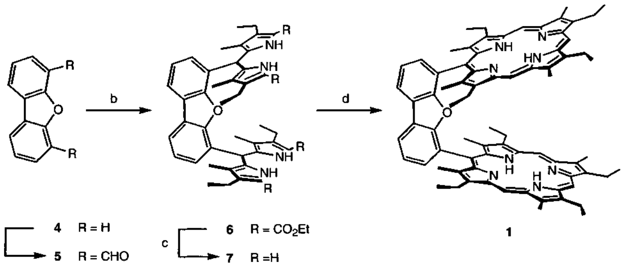
Received August 16, 1999

Cofacial bisporphyrins have drawn considerable interest due to their small-molecule reactivity.[1] In particular, a number of dicobalt derivatives catalyze the direct four-electron reduction of oxygen to water.[1−4] The two major types of cofacial bisporphyrins are those linked via two or more flexible strapping units[5−10] and pillared bisporphyrins attached by a single rigid spacer, which to date has been limited to anthracene (DPA)[1,11] or biphenylene (DPB).[1,12−14] The interplanar distance between the facially disposed subunits is of utmost importance in the systems containing flexible linkers. For example, among doubly bridged amide-linked dicobalt bisporphyrins, only the four-atom bridged species is capable of the direct four-electron reduction of oxygen.[1,3] Similar compounds with linkages of different lengths predominately mediate two-electron processes, due to the tendency of these molecules to adopt a slipped conformation with the two porphyrin rings laterally displaced.[15,16] In contrast, the more rigid pillared systems ameliorate ring slippage effects, and accordingly, dicobalt complexes of both DPA and DPB display four-electron reactivity toward oxygen.[2] This activation chemistry is observed despite the ca. 1 Å difference in interplanar metal−metal distances, leading Collman to suggest that these molecules, which have small lateral shifts, have a longitudinal "Pac-Man" flexibility that allows the binding pocket to structurally accommodate reaction intermediates during catalysis.[1] We now provide the first direct support for this crucial conformational change in a *single* framework through the synthesis and characterization of cofacial bisporphyrins anchored by a rigid dibenzofuran pillar (DPD). A comparative structural analysis of biszinc **2** and bisiron(III) μ-oxo **3** complexes demonstrates the unprecedented ability of the DPD framework to open and close its binding pocket by a longitudinal distance of over 4 Å in the presence of exogenous ligands, thus validating the predicted "Pac-Man" effect for pillared cofacial porphyrin systems.

Scheme 1[a]



[a] Conditions: (a) (1) *n*-butyllithium, hexane, reflux, (2) DMF, H_2O; (b) Ethyl 3-ethyl-4-methylpyrrole carboxylate, HCl, ethanol, reflux; (c) NaOH, ethylene glycol, reflux, 95%; (d) (1) 3,3′-diethyl-5,5′-diformyl-4,4′-dimethyl-2,2′-dipyrrylmethane, *p*-toluenesulfonic acid, methanol (2) *o*-chloranil, (3) $Zn(OAc)_2{\cdot}2H_2O$/methanol, (4) HCl.

We employ the standard three-branch strategy[11,17] for the construction of **1** (Scheme 1). Selective 4,6 dilithiation of dibenzofuran **4** followed by the sequential addition of dry DMF and water yields **5** in 50% yield. Reaction of **5** with 2-(ethyloxycarbonyl)-3-ethyl-4-methylpyrrole[18] and subsequent hydrolysis and decarboxylation affords the α-free tetrapyrrole **7** (>90% over two steps). Condensation of **7** with 3,3′-diethyl-5,5′-diformyl-4,4′-dimethyl-2,2′-dipyrrylmethane[19] in the presence of PTSA followed by *o*-chloranil oxidation gives **1** in 20% yield after workup and purification. The ^{1}H NMR spectrum of **1** is consistent with a splayed structure in solution, as the internal NH-pyrrolic resonances are only slightly upshifted (−3.85, −3.91 ppm) compared to monomeric porphyrins.

The introduction of porphyrinic substituents at the 4 and 6 positions of dibenzofuran imparts a significantly greater interplanar angle compared to other pillared bisporphyrins.[1,14,20] Zn_2(DPD) **2** is obtained from reaction of **1** with $Zn(OAc)_2{\cdot}2H_2O$. Figure 1 depicts the wedge geometry of bisporphyrin **2** with an interplanar angle of 24.6° and a large Zn−Zn distance of 7.775 Å (Ct−Ct distance 7.587 Å). The dibenzofuran bridge is planar (mean plane deviation 0.016 Å) and porphyrin macrocycles are essentially flat (average deviation 0.119 Å). The Zn(II) ions are tetracoordinate with an average Zn−N bond length of 2.042 Å. As observed for **1**, the similarity of the B band maximum (400 nm) to that of a monomer analog[21] indicates that exciton coupling between the porphyrinic chromophores in **2** is weak, suggestive of a preserved open-wedge structure in solution.

Reaction of **1** with $FeBr_2$ yields the corresponding diiron(II) complex. Exposure of this diiron(II) complex to air initially yields

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[21] Soret (B) band data for related zinc porphyrins: Zn(5(4′-Br)-Ph-2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrin), $\lambda_{max} = 405$ nm, $\epsilon = 260000$ M^{-1} cm^{-1}; Zn_2(DPA), $\lambda_{max} = 405$ nm, $\epsilon = 342000$ M^{-1} cm^{-1}; Zn_2(DPB), $\lambda_{max} = 391$ nm, $\epsilon = 300000$ M^{-1} cm^{-1}; Zn_2(DPX), $\lambda_{max} = 389$ nm, $\epsilon = 290000$ M^{-1} cm^{-1}.

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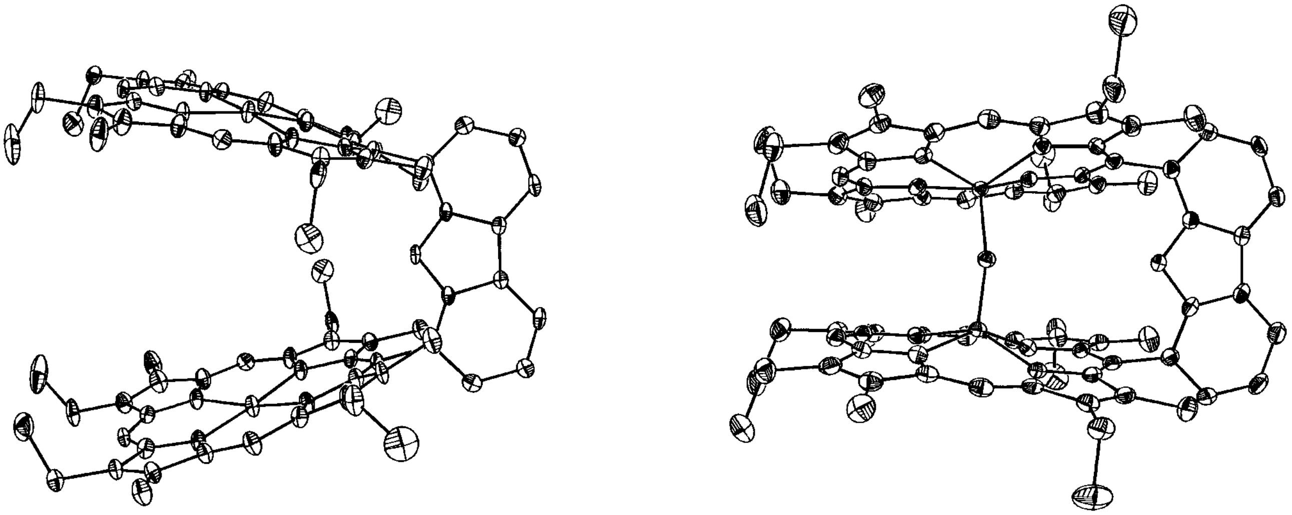

2 **3**

Figure 1. Molecular structures of **2** and **3** with hydrogen atoms omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

intra- and intermolecular μ-oxo complexes as evidenced by TLC. The two products are equilibrated upon treatment with basic alumina to afford only the *intramolecular* bis-Fe(III) μ-oxo complex **3**. The structure of **3** (Figure 1) clearly demonstrates the dramatic ability of the DPD system to "bite" down on exogenous ligands. The porphyrin *meso* carbons connected to the bridge bend inward, forming a dihedral angle of 12.8°, while the macrocyclic cores tilt inward by 10.1°. As a result, the Fe−Fe distance is reduced to 3.504 Å, with a Ct−Ct distance of 4.611 Å. Average Fe−O (1.782 Å) and Fe−N (2.104 Å) bond lengths are normal for bisiron(III) μ-oxo porphyrins.[22−24] The dibenzofuran bridge deviates from planarity, forming a dihedral angle of 9.8° between the two phenyl rings, and is positioned with dihedral angles of approximately 84° with the porphyrin cores.

Several other structural features of **3** merit comment. Conformational analysis indicates that the S_4-ruffled porphyrin cores are structurally inequivalent in the solid state,[25,26] as core **1** displays a smaller displacement from planarity ($d_{avg} = 0.0678$ Å) than core **2** ($d_{avg} = 1.1063$ Å). The Fe atom displacements from the porphyrin mean planes (0.621 and 0.678 Å for Fe1 and Fe2, respectively) are considerably larger than those for related systems.[22−24] Unlike most other μ-oxo bisiron porphyrins, where the rings align staggered to maximize π interactions,[25] the rigid dibenzofuran spacer restricts the porphyrin cores from rotation with respect to each other, resulting in an eclipsed conformation with an average N−Fe1−Fe2−N torsion angle of 1.65°. Perhaps the most striking feature of the structure of **3** is the small, bent Fe−O−Fe angle of 158.7°. For most iron μ-oxo porphyrins, the Fe−O−Fe unit is nearly linear with angles ranging from 172 to 179° to minimize the nonbonded interactions between the porphyrinic cores.[22,24] For comparison, the smallest Fe−O−Fe angle reported thus far, in a urea-linked bisporphyrin (161.1°), was due to hydrogen bonding of the central oxygen to two solvent water molecules.[27]

The preference of intramolecular μ-oxo complex **3** over intermolecular products suggests that the longitudinal open-to-closed conformational change for DPD is accompanied by a small energy. An accessible pocket that can collapse about a guest with minimized conformational energy should lower the transition state energy for substrate activation. Accordingly, DPD provides an attractive platform for our investigations of proton-coupled, multielectron activation of small molecules.[28] Indeed, preliminary experiments with the dicobalt derivative show that this complex efficiently catalyzes the four-electron reduction of oxygen to water on a graphite electrode.[29] Further investigation of the application of the DPD ligand is under way.

Acknowledgment. C.J.C. gratefully acknowledges the National Science Foundation for a predoctoral fellowship. We thank Alan Heyduk for help with the X-ray crystallography. This work was supported by the National Institutes of Health GM 47274.

Supporting Information Available: Characterization data and detailed descriptions of syntheses of all compounds, X-ray crystallographic data for **2** and **3** including complete crystallographic experimental details, tables of bond distances and angles, positional parameters for all atoms, equivalent isotropic displacement parameters, anisotropic displacement parameters, and additional ORTEP views with full atom labeling schemes for **2** and **3** (PDF). X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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