Transition-Metal-Mediated [2 + 2 + 2] Cycloaddition Reactions with Ethyne-Containing Porphyrin Templates: New Routes to Cofacial Porphyrin Structures and Facially-Functionalized (Porphinato)metal Species

James T. Fletcher and Michael J. Therien*

Department of Chemistry
University of Pennsylvania
Philadelphia, Pennsylvania 19104-6323

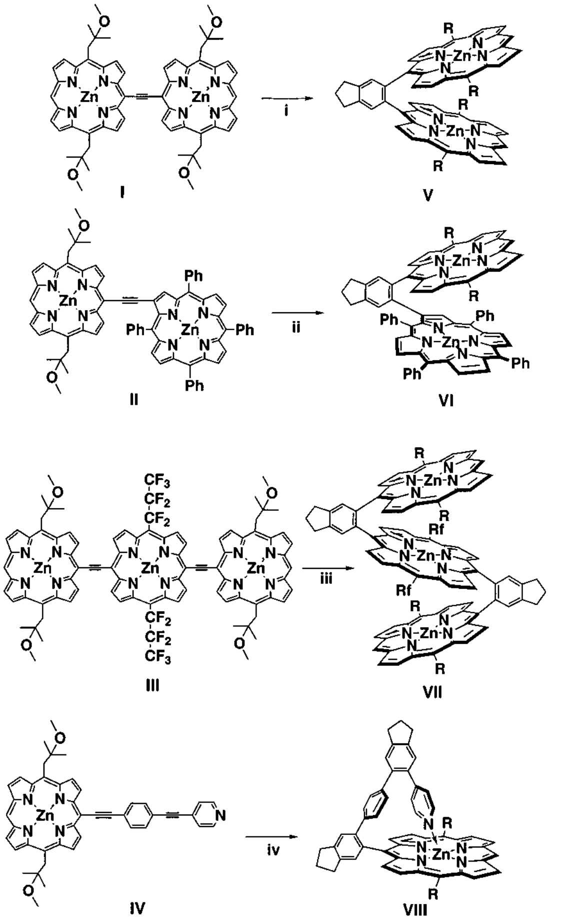
Received January 14, 2000
Revised Manuscript Received August 21, 2000

The diverse reaction chemistry generated by the limited number of metalloenzyme catalytic motifs arises from rigorous definition of active-site environments by the protein matrix. Rigidly fixing the spatial arrangement of metal ligands and the relative proximity of electronically disparate transition-metal centers thus constitute challenging aspects of biologically inspired catalyst design. In this report, we exploit the finesse of metal-mediated cycloaddition reaction chemistry to build well-defined (porphinato)metal structures.[1,2] An exemplary set of such reactions is described that utilize alkyne-elaborated porphyrinic reactants, demonstrating that such transformations offer new opportunities for engineering catalytic, chromophoric, and supramolecular properties of structures based on these macrocycles.

Metal-catalyzed cross-coupling reaction schemes[3,4] provide straightforward entry into both monomeric and oligomeric porphyrin-based structures that feature augmented conjugation.[5,6] As such, ethyne-containing porphyrinic cycloaddition templates **I**−**IV** were prepared readily from appropriately halogenated (porphinato)zinc(II) species;[4,5] Scheme 1 highlights the products formed when **I**−**IV** are reacted with 1,6-heptadiyne in the presence of $Co_2(CO)_8$.[7]

Reaction of **I**−**III** under the conditions described in Scheme 1 constitutes a powerful new route into cofacial porphyrin compounds. Since the first reports of these remarkable species,[8] only minor methodological advancements have been made with respect to the conventional pyrrole and aldehyde condensation routes to rigidly linked cofacial porphyrin structures;[9] this has both limited the range of electronic structural modifications possible in such constructs and required considerable synthetic effort to build related, rigid face-to-face structures that comprise more than two porphyrin units.[10]

Scheme 1. Examples of Co-Mediated [2 + 2 + 2] Cycloaddition Reactions of Ethyne-Containing Porphyrin Structures with 1,6-Heptadiyne[a]



[a] Reagents and conditions: 4:1 toluene:dioxane, 100 °C. (i) **I** (67 μmol), 1,6-heptadiyne (670 μmol), $Co_2(CO)_8$ (134 μmol), (87%); (i) **II** (43 μmol), 1,6-heptadiyne (430 μmol), $Co_2(CO)_8$ (86 μmol), (85%);(iii) **III** (25 μmol), 1,6-heptadiyne (500 μmol), $Co_2(CO)_8$ (100 μmol), (87%);(iv) **IV** (64 μmol), 1,6-heptadiyne (1.28 mmol), $Co_2(CO)_8$ (128 μmol), (64%). Experimental details available as Supporting Information.

Meso-to-*meso* ethyne-bridged **I** serves as a precursor to **V**, which features a ligand motif closely related to the 1,2-diporphyrylphenylene frameworks shown by Naruta to support metal-catalyzed homogeneous oxidation of water.[11] An X-ray crystallographic structure of **V**·$(MeOH)_2$ is shown in Figure 1. Interestingly, Osuka has reported the structure of 1,2-bis[5′-(15′-(*p*-tolyl)porphinato]zinc(II)]benzene, which features coplanar (porphinato)zinc(II) units that manifest a minimal 3.43 Å average

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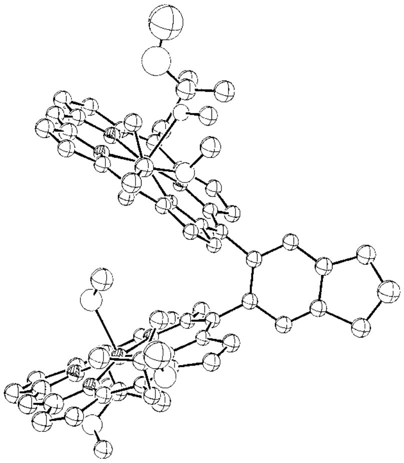

Figure 1. ORTEP view of compound **V**$\cdot$(MeOH)$_2$ with thermal ellipsoids at 30% probability.

interplanar separation distance.[9a] **V**$\cdot$(MeOH)$_2$ thus constitutes an open-structure analogue of Osuka's 1,2-diporphyrylphenylene complex having a cavity-bound, hydrocarbon-based small molecule redox substrate. Key metrical parameters of **V**$\cdot$(MeOH)$_2$ include a Zn−Zn distance of 6.54 Å, a large 56.4° dihedral angle between least-squares planes defined by the four central nitrogen atoms of its respective (porphinato)zinc(II) units, and a substantive lateral shift[12] between the two porphyryl zinc atoms of 3.66 Å. Importantly, the **V**$\cdot$(MeOH)$_2$ structure underscores: (i) that even when (porphinato)metal species are held in a cofacial arrangement by a 1,2-phenylene bridge, the structural plasticity necessary to accommodate both substrates and intermediates in catalytic redox cycles is clearly inherent, and (ii) that the energies required to distort a rigid, cofacial bis[(porphinato)metal] compound into the open "Pac-Man" structure[13] are no more than that provided by axial ligation and crystal packing forces.[14]

The conversion of **II** to **VI** exemplifies the capacity of metal-templated cycloaddition reactions to assemble new classes of such structures, producing the first example of a covalently bridged, conformationally well-defined cofacial bis(porphyrin) system featuring *meso*-to-β connectivity. While conventional face-to-face porphyrin structures that feature macrocycles linked to a rigid bridge via their respective *meso*-carbon positions display excitonic interactions in the B-band region when the interplanar separations are not unduly large, the oscillator strength of the low-energy B-state exciton component is modest due to its formally dipole forbidden nature. Because the *x*- and *y*-polarized B-states of a given (porphinato)zinc(II) unit in **VI** are rigorously precluded from being superimposable with the analogous *x*′- and *y*′-polarized states of the (porphinato)zinc(II) unit held cofacial to it, the low-energy exciton band displays dramatically enhanced intensity in comparison to *meso*-to-*meso* bridged bis(porphyrin) compounds (Supporting Information).

The use of tris[(porphinato)zinc(II)] complex **III** as a starting material for these for these Co-assisted cycloadditions demonstrates that new cofacial porphyrin prototypes can be accessed in a straightforward manner and that substantial variation in macrocycle electronic structure does not limit the scope of such reactions. Compound **VII** is an example of a newly defined class of conjugated porphyrin arrays in which adjacent (porphinato)-metal units differ substantially with respect to their electronic structure;[15] potentiometric analysis shows that [5,15-di(perfluoroalkyl)porphinato]zinc(II) species possess HOMOs and LUMOs that are uniformly lowered in energy by ~0.33 V relative to their conventional, electron-rich counterparts.[15,16] Congruently, **VII**'s optical spectrum shows clear evidence of charge resonance character in the prominent absorption bands, and photophysical behavior consistent with low-lying charge-transfer states.[17]

Co-assisted cycloaddition of **IV** and 1,6-heptadiyne produces **VIII**, a complex that differs markedly from other previously delineated examples of (porphinato)metal species that feature covalently attached axial ligands.[18] Because the metal-bound axial pyridyl moiety of **VIII** is linked directly to the macrocycle via an entirely aromatic structure, the conformation of the multidentate ligand is highly restricted (Supporting Information). Such coordination environments built via two successive metal-templated cycloaddition reactions define a potential approach to control rigorously metal-centered redox potential and d orbital occupancy,[19] as well as a synthetic strategy to be exploited in heme protein bioinorganic chemistry.

Metal-templated cycloaddition reactions involving appropriately elaborated porphyrinic synthons not only define new routes to facially functionalized (porphinato)metal species and cofacial porphyrin structures; they provide a new means to modulate optical and electronic properties within these structural motifs. With respect to this latter class of compounds, it is important to note that because palladium-catalyzed cross-coupling of ethyne- and halogen-bearing porphyrin templates makes straightforward the syntheses of heterobimetallic, electron-rich, electrophilic, and electronically asymmetric ethyne-bridged bis(porphyrin) systems,[5a,b,15] sequential cross-coupling/cycloaddition reactions enable the construction of entirely new classes of cofacial porphyrin species; such structures will make manifest numerous new opportunities with respect to redox catalyst design.[13,20]

Acknowledgment. M.J.T. is indebted to the Office of Naval Research (N00014-98-1-0187) for their generous support of this work and gratefully acknowledges the Camille and Henry Dreyfus Foundation for a research fellowship. J.T.F. thanks the International Precious Metals Institute (IPMI) for a graduate student research award. The structure of compound V was determined by Dr. Patrick Carroll (X-ray Facility, Department of Chemistry, University of Pennsylvania).

Supporting Information Available: Characterization data, optical spectra, and detailed syntheses of compounds IV−VIII, along with tables of crystal data for compound **V** (PDF). An X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) (a) The B-state spectral breadth of **VII** is enhanced with respect to appropriate spectroscopic benchmarks. Compound (λ_{max} B band, fwhm): **VII** (405 nm; 1227 cm^{-1}); [5,15-bis[5′-(6′-phenylindanyl)]-10, 20-bis(heptafluoropropyl)porphinato]zinc(II) (421 nm; 775 cm^{-1}); 5-(5′-[10′,20′-di(2-methoxy-2-methylpropyl)porphinato]zinc(II))-6-phenylindane (421 nm; 622 cm^{-1}). See Supporting Information.

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