

Collapsed Molecular Rectangles Based on Rhenium(I) Coordination of Ethynylpyridyl Porphyrins – Synthesis, Structure, and Bending-Induced Charge-Transfer Behavior

Kurt D. Benkstein,^[a] Charlotte L. Stern,^[a] Kathryn E. Splan,^[a] Robert C. Johnson,^[a] Keith A. Walters,^[a] Frederick W. M. Vanhelmont,^[a] and Joseph T. Hupp^{*[a]}

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Efforts to synthesize extremely large rectangle-shaped porphyrin systems have yielded an unusual and unexpected collapsed structure that brings the porphyrin walls into van der Waals contact. The bent geometry of the nominally rigid ethynylpyridyl porphyrin ligand edges, mandated by the collapse of the rectangle, imparts significant charge-transfer character to the rectangles' Soret and Q-region electronic transitions, as shown experimentally by Stark spectroscopy

and transient DC photoconductivity measurements, and replicated by electronic structure calculations. In contrast to lower symmetry porphyrin-like pairs found in naturally occurring photosystems, however, the light-induced charge transfer is an intra-porphyrin rather than inter-porphyrin process.

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Introduction

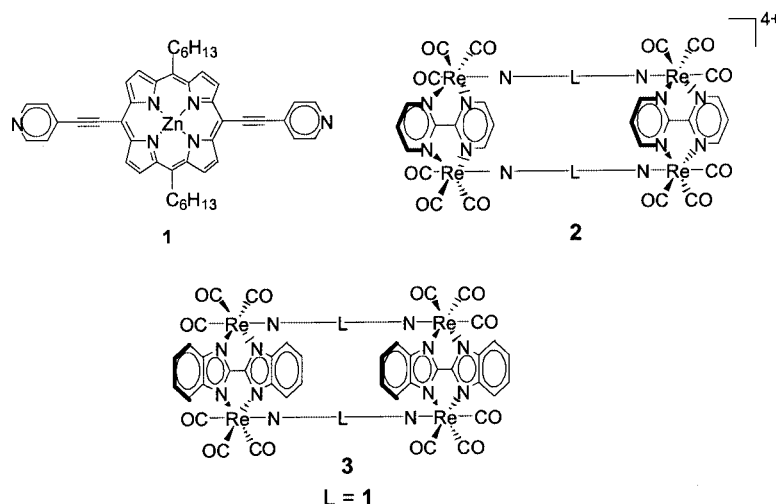
Cyclic molecular host compounds — squares, triangles, pentagons, hexagons, cylinders, prisms and other structures — featuring transition-metal-ion corners and multifunctional aromatic ligands as edges hold substantial promise for applications entailing selective chemical sensing, reaction catalysis, or nanoscale molecular transport.^[1] As a logical next step beyond the now ubiquitous molecular-square motif, we recently reported the synthesis of tetrametallic molecular rectangles featuring frameworks of modest size: ca. $6 \times 11 \text{ Å}$.^[2,3] The resulting cavities are too narrow to host even a planar aromatic guest molecule. Nevertheless, by packing in a fashion that creates intermolecular cavities, neutral versions of the rectangles have proven effective in the solid state as hosts for selected volatile organic chemical guests (arenes)^[2b] and as shape-selective thin-film coatings for condensed-phase molecular transport.^[4] Here we describe the synthesis of new and much larger rectangles **2** and **3** featuring lengthy dihexyl derivatives of [5,15-bis(4-ethynylpyridyl)porphyrinato]zinc(II) (**1**) as walls. Intermolecular voids, potentially suitable for guest uptake, were again expected in the solid state. Additionally, however, our hope was that the extended walls would prove sufficiently flexible, especially in solution, to permit the rectangles to encapsulate polyaromatic guests in an intramolecular fashion. We further envisioned that the available pair of zinc

sites could be used to bind a difunctional ligand axially, thereby propping open the porphyrin walls and resulting in a well-defined, but smaller, cavity. We instead found that the cavities are collapsed such that the porphyrinic walls approach within van der Waals distances and that the collapsed cavities strongly resist functionalization via Zn^{II} ligation. In addition we found that the cavity collapse alters the rectangle's electronic structure and imparts significant porphyrin-localized charge-transfer character to both B- and Q-band transitions, as evidenced by electronic Stark effect (electroabsorption) measurements, transient DC photoconductivity measurements, and electronic structure calculations.

Results and Discussion

Reaction of **1** with either $[\text{Re}_2(\text{CO})_6\text{Cl}_2(\mu\text{-bipyrimidine})]$ or $[\text{Re}_2(\text{CO})_8\{\mu\text{-bis}(\text{benzimidazolate})\}]$ leads readily to the desired rectangles **2** and **3**.^[5] The single-crystal X-ray structure for **3** is shown in Figure 1. Especially striking is the pronounced inward bowing of two of the four ethynylpyridine linkages (15.6° angle between the plane of the pyridine and the plane of the porphyrin + second pyridine). Thus, while the rhenium atoms define a framework 24.6 Å long and 5.7 Å wide, the porphyrins approach within 3.4 Å , slightly less than the estimated van der Waals contact distance (3.6 Å). A "top" view of the structure shows that the porphyrins are significantly laterally slipped — the zinc centers, for example, being laterally displaced from each other by 1.0 Å to give a slip angle of 19° . This offset is consistent with strong porphyrin/porphyrin π -stacking in-

^[a] Department of Chemistry and Center for Nanofabrication and Molecular Self-Assembly, Northwestern University
2145 Sheridan Road, Evanston, IL, 60208, USA
Fax: (internat.) +1-847/491-7713
E-mail: jthupp@chem.nwu.edu



teractions and is similar to the displacements reported for other cofacial metalloporphyrin assemblies.^[6] Another factor may be an intrinsic predisposition at the rhenium center for angles of less than 90° between the chelating short-edge ligand and the Re–N(imine) bond; crystal structures of closely related Z-shaped molecules such as *trans*–[(pyridine)₂Re₂(CO)₈{μ-bis(benzimidazolate)}] feature angles of 82 to 84°.^[7]

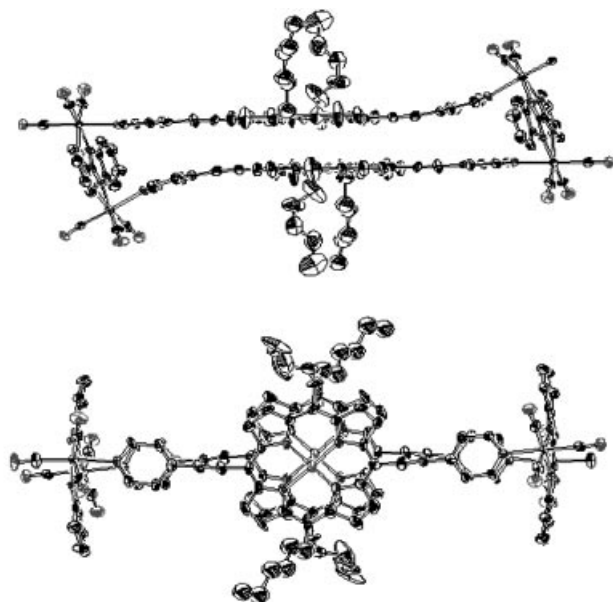


Figure 1. ORTEP representations of **3** showing the side view (top) and top view (bottom) of the co-facial porphyrin systems; hydrogen atoms have been omitted for clarity; the thermal ellipsoids represent 50% occupancy

While the collapsed cavity is too narrow for guest incorporation, as evidenced by the crystal structure, we reasoned that the flexible nature of the porphyrin walls may allow for cooperative interior binding of a single bridging ligand by the pair of Zn^{II} centers. To this end, DABCO (1,4-diazobicyclo[2.2.2]octane), a strong Lewis base, might be expected to bind inside the cavity despite being larger than the frame-

work defined by the rhenium corners. However, DABCO is observed to bind to **3** in a 2:1 stoichiometry with no detectable preferential binding of the first equivalent ($K_b = 5 \times 10^4 \text{ M}^{-1}$ in CHCl₃) — an observation that clearly implies exterior binding. Furthermore, quinuclidine, a monofunctional, exterior-binding ligand also binds to **3** in a 2:1 stoichiometry, with $K_b = 2 \times 10^5 \text{ M}^{-1}$, four times larger than the binding constant of DABCO. With other bis(porphyrinato)zinc(II) systems, the di-functionality of DABCO can favor inside binding (double ligation of a single ligand) over outside binding by as much as 300-fold, despite estimated π -stacking enthalpies of as great as -48 kJ mol^{-1} .^[8] The absence of significantly favored inside binding suggests, but does not prove, even greater interactions here.

The visible-region electronic absorption spectra for **2** and **3** are dominated by porphyrin-based B- and Q-bands (Figure 2). In particular, the Q-bands for **2** and **3** are red-shifted by 20 and 10 nm, respectively, versus the Q-band for **1**, consistent with expected electron-withdrawing effects due to metal-cation coordination. Electroabsorption measurements at 77 K for **3** in a 2-methyl-THF glass (Figure 3) show that excitation in either region entails charge transfer.

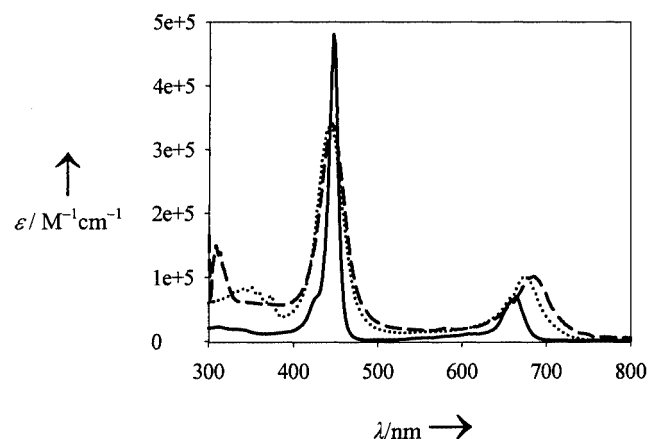


Figure 2. Electronic absorption spectra of **1** (—), **2** (---), and **3** (···) in CHCl₃

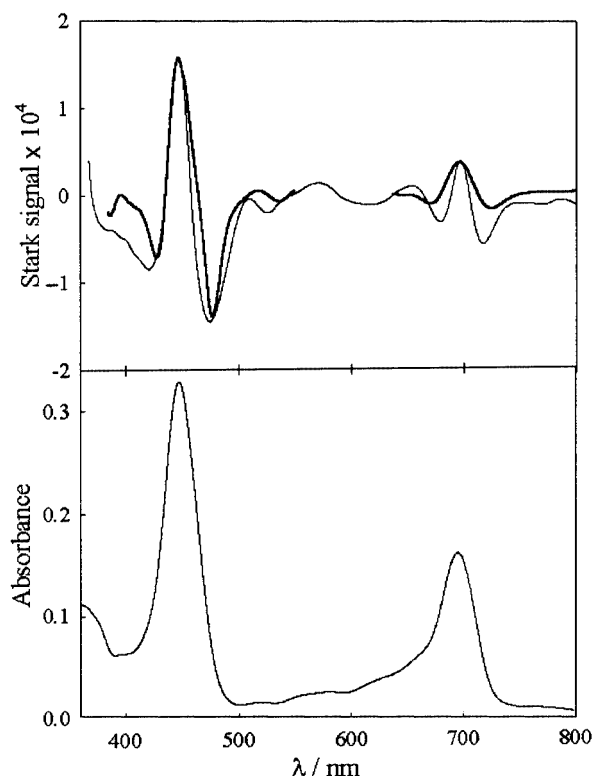


Figure 3. Electroabsorption (Stark) spectrum (top) at 77 K for **3** in a 2-methyl-THF glass at a field strength (r.m.s.) of 4.5×10^7 V/m; both B- and Q-regions of the Stark spectrum display substantial components of the second derivative (bold line) of the absorption spectrum, indicating charge-transfer character in these regions; dipole moment changes were obtained by fitting the spectra to appropriately weighted sums of zeroth-, first-, and second derivative spectra

A standard Liptay analysis of the electroabsorption spectrum,^[9] neglecting local field corrections, yields ground-state to excited-state vector-dipole-moment changes, $|\Delta\mu|$, of 5 debye for the B transition and 2 debye for the Q transition. No charge transfer is seen in Stark measurements of **1**. That the charge-transfer observation is not peculiar to the glass environment is evidenced by liquid-phase transient DC photoconductivity measurements^[10] (not shown) that demonstrate that the scalar dipole moment of the emissive excited state of **3** exceeds that of the ground state.

It is tempting, by analogy to the known low-energy charge-transfer behavior of various versions of the bacterial-chlorophyll dimer (the “special pair”) in photosynthetic reaction systems, to ascribe this unusual electric-field-effect behavior to photo-induced porphyrin-to-porphyrin charge-transfer. Nevertheless, the result would be most surprising given the inversion symmetry of **3**.^[11] A comparison of Stark measurements made at electric-field/electromagnetic-field angles of 55° and 90° shows that in both the B- and Q-regions the change in dipole moment (charge-transfer vector) is essentially collinear with the transition dipole moment (absorption vector). This unequivocally rules out por-

phyrin-to-porphyrin charge-transfer, for which a vector offset of close to 90° would be expected. The behavior instead is ascribed to the remarkable structural distortions occurring in one of the two ethynylpyridines attached to each porphyrin. Bending partially attenuates electron withdrawal by the rhenium-cation-appended linkage, thereby reducing the symmetry of the porphyrin in an electronic sense and creating a porphyrin-localized dipole moment. AM1 calculations (HyperChem. 5.02), using a bent and doubly-pyridyl-protonated ligand **1** as a surrogate for one-half of **3** (in the absence of parameters for Re), corroborate the explanation. The anti-parallel arrangement of the porphyrins, of course, leads to a net molecular dipole moment of zero in the ground electronic state. Local excitation of only one of the two available porphyrins eliminates the inversion symmetry, leaving **3** with a calculated net charge-transfer polarization of 2 debye in the lowest singlet excited state.

Finally, ambient temperature photo-excitation of **1**, **2**, and **3** in THF leads to singlet emission. Corrected emission maxima are red-shifted for the rectangles in comparison to free porphyrin: $\lambda_{em}(\mathbf{1}) = 677$ nm, $\lambda_{em}(\mathbf{2}) = 694$ nm, $\lambda_{em}(\mathbf{3}) = 714$ nm. Emission lifetimes are: $\tau(\mathbf{1}) = \tau(\mathbf{2}) = 1.3$ ns, with emission too weak for reliable assessment of $\tau(\mathbf{3})$. Cyclic voltammetry in THF yielded the following reversible reduction potentials, measured vs. Ag/AgCl, for **1**: -0.96 and -1.39 V; for **2**: -0.70 , -0.95 , -1.06 , -1.18 V; and for **3**: -0.89 , -1.08 , and -1.20 V. All are assigned as porphyrin reductions, except the first and fourth reductions for **2**; these are multi-electron reductions and are assigned as overlapping one-electron reductions of the widely separated pair of bipyrimidine ligands.^[12] The relatively good reductive accessibility of the coordinated bipyrimidine edges suggests redox quenching and may account for the attenuation of the fluorescence of **2**. The splitting of nominally equivalent one-electron porphyrin reduction waves, on the other hand, suggests significant $\text{Por}^-/\text{Por}^-$ electrostatic repulsion and/or $\text{Por}^-/\text{Por}^0$ electronic interactions. Combining the voltammetry and emission data, the estimated excited-state reduction potentials for **1** and **3** are both approximately $+0.87$ V; with less certainty, because of the intervening bipyrimidine reduction, the excited-state reduction potential for **2** is approximately $+0.82$ V.

To summarize, coordination chemistry based molecular-rectangle construction using lengthy bis(4-ethynylpyridyl)-porphyrins as two of the edges yields an unusual collapsed structure that places the porphyrin faces in very close proximity and substantially distorts two of the four nominally rigid ethynylpyridyl linkages. These distortions, in turn, polarize the porphyrins sufficiently that electronic transitions in both the B- and Q-band regions develop significant charge-transfer character. While we have emphasized here the special structural and photophysical features of the new rectangles, there are also interesting prospects for chemical catalysis, particularly if reactive metals are used in place of zinc and if added oxidizing or reducing equivalents lead to porphyrin-porphyrin electrostatic repulsion, thereby opening up the collapsed cavity for substrate binding.

Experimental Section

General: $[\text{Re}_2(\text{CO})_6\text{Cl}_2(\mu\text{-bipyrimidine})]^{[2a]}$ $[\text{Re}_2(\text{CO})_8\{\mu\text{-bis}(\text{benzimidazolates})\}]^{[2b]}$ and **1**^[13] were synthesized according to literature methods. THF was dried with Na/benzophenone. All other chemicals and solvents were reagent grade and used as received. ¹H NMR spectra were recorded with a 400 MHz Varian Mercury spectrometer. FAB mass spectra were obtained in the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois. Electroabsorption experiments were performed at 77 K in neat 2-methyltetrahydrofuran glass with a Cary-14 spectrophotometer. Full experimental procedures and the data reduction method have been described in detail elsewhere.^[14]

1: ¹H NMR ($[\text{D}_5]\text{pyridine}/\text{CDCl}_3$): δ = 1.04 (t, J = 7 Hz, 6 H), 1.45 (m, 4 H), 1.59 (m, 4 H), 2.65 (m, 4 H), 5.13 (t, 4 H), 8.03 (d, J = 6 Hz, 4 H), 8.98 (d, J = 6 Hz, 4 H), 9.79 (d, J = 5 Hz, 4 H), 10.05 (d, J = 5 Hz, 4 H) ppm. LR ES-MS: calcd. for $[\text{M} + \text{H}^+]$: m/z = 743; found 743. HR FAB-MS: calcd. for $[\text{M} + \text{H}^+]$: m/z = 743.2841; found 743.2840. UV/Vis (THF): λ_{max} = 446, 664 nm.

2: Porphyrin rectangle **2** was formed by first refluxing 15.5 mg (0.0201 mmol) of $[\text{Re}_2(\text{CO})_6\text{Cl}_2(\mu\text{-bipyrimidine})]$ with slightly more than two equivalents of AgOTf (10.9 mg, 0.0424 mmol) in 20 mL of acetone under N_2 for 4 hours. The solution was passed through celite and concentrated to leave a red film. This film, $[\text{OTf}(\text{CO})_3\text{Re}]_2(\mu\text{-bipyrimidine})$, was refluxed for two days with 14.8 mg (0.0199 mmol) of **1** in 20 mL of deoxygenated THF. The desired product precipitated as a dark red powder (11.3 mg, 0.0032 mmol) in 33% yield. ¹H NMR ($[\text{D}_6]\text{DMSO}$): δ = 0.088 (t, J = 7 Hz, 12 H), 1.31 (m, 16 H), 1.57 (m, 8 H), 1.94 (m, 8 H), 4.28 (m, 8 H), 7.98 (d, J = 6 Hz, 8 H), 8.52 (d, J = 6 Hz, 8 H), 8.66 (m, 12 H), 9.06 (d, J = 4 Hz, 8 H), 10.16 (d, J = 6 Hz, 8 H) ppm. LR ES-MS: calcd. for $[\text{M} - 2\text{OTf}]$: m/z = 1592.0; found 1591.6. UV/Vis (THF): λ_{max} = 446, 686 nm.

3: Equimolar amounts of $[\text{Re}_2(\text{CO})_8\{\mu\text{-bis}(\text{benzimidazolates})\}]$ (22.2 mg, 0.0268 mmol) and **1** (25.5 mg, 0.0255 mmol) were refluxed in 30 mL of THF for two days. Upon addition of hexanes the desired product precipitated as a dark green powder (35.4 mg, 0.0117 mmol) in 91% yield. ¹H NMR (CDCl_3): δ = 0.879 (t, J = 7 Hz, 12 H), 1.32 (m, 16 H), 1.55 (m, 8 H), 1.92 (m, 8 H), 4.34 (t, J = 8 Hz, 8 H), 7.50 (d, J = 6 Hz, 8 H), 7.60 (q, J = 3 Hz, 8 H), 8.04 (q, J = 3 Hz, 8 H), 8.24 (d, J = 6 Hz, 8 H), 8.66 (d, J = 5 Hz, 8 H), 8.92 (d, J = 5 Hz, 8 H) ppm. FTIR (CHCl_3): ν_{CO} = 1901, 1922, 2022, 2028 cm^{-1} ; ν_{CC} = 2188 cm^{-1} . LR FAB-MS: calcd. m/z = 3034.0; found 3033.4. UV/Vis (THF): λ_{max} = 444, 686 nm. X-ray quality crystals of **3** were grown by slow evaporation from a THF/toluene solution (1:1, v:v) at ambient temperature.

Crystal Data for 3-4C₇H₈: $\text{C}_{150}\text{H}_{74}\text{N}_{20}\text{O}_{12}\text{Zn}_2\text{Re}_4$; crystal dimensions $0.5 \times 0.20 \times 0.48$ mm; triclinic; space group $P\bar{1}$ No. 2; a = 10.877 (2), b = 17.501 (2), c = 19.230 (3) Å, α = 88.657 (2)°, β = 82.615 (2)°, γ = 88.943 (2)°, V = 3628.6 (8) Å³; Z = 1; $\rho_{\text{calcd.}}$ = 1.487 g cm⁻³; $2\theta_{\text{max}}$ = 56.8°; Mo- K_α radiation, λ = 0.7101 Å; T = 153 K; 33040 reflections, of which 16692 were unique; 9224 of these were included in the refinement; data corrected for Lorentz polarization effects; solution by direct methods (G. M. Sheldrick, SHELX 1997) and refinement on $|F^2|$ by full-matrix least-squares procedures (TeXsan for Windows version 1.03, Molecular Structure Corporation, Texas, USA); 781 parameters; isotropic refinement of disordered solvent molecules and C61–C66, the remaining non-hydrogen atoms were refined anisotropically; methyl groups for toluene and half the disordered hexyl group were not found in the difference Fourier map. H atoms were included, except in

disordered solvent molecules and the constrained carbons, but not refined; R = 0.063, R_w = 0.141.

CCDC-176672 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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