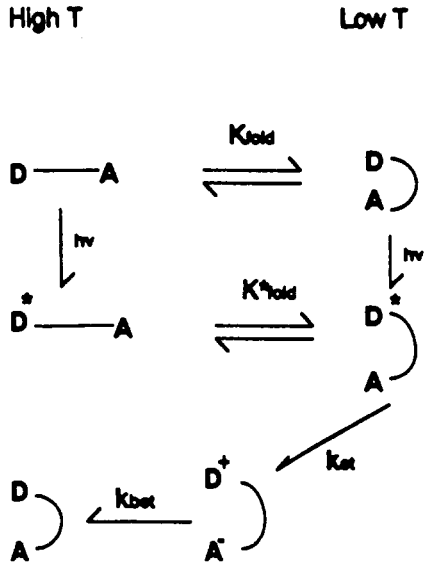
Scheme I



nitrobenzene protons *a* and *b* reveals significant coupling to bipyridyl protons *c*, *d*, and *e*. At 298 K, the cross polarizations are absent. Evidently, ground-state **1** exists in a folded form at the lower temperature and unfolded forms at higher temperatures. Additional NMR experiments reveal a deshielding of pyridyl proton *f* with decreasing *T*, implying that the macrocyclic spacer is substantially flexed near the py functionality upon folding. X-ray crystallography with a related assembly featuring crown attachment to *bi*pyridine shows that a stable folded structure with an offset rather than a cofacial bpy/nitrobenzene configuration can be formed.[8] The exact nature of the analogous folded py/nitrobenzene configuration obtained here is unclear;[9] however, on the basis of the observed insensitivity of the Re^{I}py emission energy to conformational form, a cofacial configuration can probably again be ruled out.

Returning to Figure 1, we propose (Scheme I) that the actual ET step occurs, in both temperature regimes, from a folded geometry. At high temperatures ($T > 280$ K) this would require an "uphill" conformational change as a preceding step.[10] If the conformational change occurs in a preequilibrium fashion, then the differences in activation parameters between the two temperature regimes would describe the thermodynamics of the excited-state folding step.[11] On this basis, we obtain $\Delta H°_{folding} = -7.5$ kcal mol^{-1} and $\Delta S°_{folding} = -27$ eu.[12] Alternatively, the folding step might be kinetically slow; the overall kinetics could then be viewed as conformationally gated, in much the same sense as was recently proposed for certain metalloprotein redox systems.[13,14] In any case, the overall kinetic incentive for ET via an uphill (at high *T*) folding sequence almost certainly must be avoidance of the extreme nonadiabaticity (and therefore, extreme inefficiency) likely connected with an open conformation pathway.

Our current efforts are focused on: (1) evaluating the solvent dependence of folding (in part as a means for understanding the nature of the forces driving the folding) and (2) controlling folding by cation encapsulation. Evidently because of its net positive charge, **1** is ineffective for cation binding. Related neutral assemblies based ion bispyridyl, chloro (rather than bipyridyl, pyridyl) coordination *are* effective,[16] however, and should be capable (like **1**) of engaging in photoinduced electron transfer.

Acknowledgment. We thank the National Science Foundation (CHE-8921590) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. J.T.H. also acknowledges a Dreyfus Teacher-Scholar Award (1991–6) and a fellowship from the Alfred P. Sloan Foundation (1990–2). The 600-MHz NMR Facility used for NOE studies was funded by the W. M. Keck Foundation (Grant 891040), NIH Shared Instrumentation Program (Grant 1 S10 RR05880), National Science Foundation Instrumentation and Instrument Development Program (Grant 8908093), State of Illinois Technology Challenge Grant Program (Grant 90-82115), and Northwestern University.

(7) A reviewer has suggested that the observed conformational change might be driven by temperature-dependent ion-pairing effects. While ion pairing in methylene chloride cannot be ruled out at the concentration levels used in the kinetics experiments (ca. 10 μM), it can be disregarded in higher dielectric solvents. On the basis of similar biphasic activation parameter plots recently obtained (unpublished) in acetonitrile and other high polarity solvents, therefore, we regard the ion-pairing explanation as insufficient to account for our findings.

(8) Absi, M. P.; Yoon, D. I., unpublished work.

(9) Nevertheless, a speculative assignment, consistent with both the preliminary NOE and electronic absorption[6]/emission data, would be an edge-(bpy)-to-face(NB) configuration.

(10) For an example of folding *after* photoinduced ET, see: Brouwer, A. M.; Mout, R. D.; Maasen van den Brink, P. H.; van Ramesdonk, H. J.; Verhoeven, J. W.; Jonker, S. A.; Warman, J. M. *Chem. Phys. Lett.* **1991**, *186*, 481.

(11) For Scheme I it can easily be shown that: $\Delta H_{ET}^{\ddagger}$ (high *T*) = $\Delta H_{ET}^{\ddagger}$ (low *T*) + $\Delta H°_{folding}$, and $R \ln A_{ET}$(high *T*) = $R \ln A_{ET}$(low *T*) + $\Delta S°_{folding}$. (Note that the low-temperature ET kinetics are effectively *de*coupled from the folding process.)

(12) In a previous report,[4] observation of a small preexponential factor for electron transfer within **1** was taken as evidence for strongly nonadiabatic behavior. While ET for **1** in unfolded form (i.e., the probable form in ref 4) is almost certainly nonadiabatic, A_{ET} (in view of Scheme I) does not provide a direct, quantitative measure of the degree of nonadiabaticity. Instead, the parameter reflects the entropic demands (either kinetic or thermodynamic) associated with folding to an electronically more favorable form.

(13) (a) Liang, N.; Pielak, G. J.; Mauk, A. G.; Smith, M.; Hoffman, B. M. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 1249. (b) Hoffman, B. M.; Ratner, M. A. *J. Am. Chem. Soc.* **1987**, *109*, 6237. (c) Hoffman, B. M.; Ratner, M. A.; Wallin, S. A. *ACS Adv. Chem. Ser.* **1990**, *226*, 125. (d) Hoffman, B. M.; Natan, M. J.; Nocek, J. M.; Wallin, S. A. *Struct. Bonding* **1991**, *75*, 86. (e) McLendon, G.; Pardue, K.; Bak, P. *J. Am. Chem. Soc.* **1987**, *109*, 7540. (f) Brunschwig, B. S.; Sutin, N. *J. Am. Chem. Soc.* **1989**, *111*, 7454. (g) Isied, S. S. *ACS Adv. Chem. Ser.* **1991**, *228*, 229. (h) Bechtold, R.; Kuehn, C.; Isied, S. S. *Nature* **1986**, *322*, 286.

(14) In principle, the two possibilities could be distinguished by examining the dependence of the kinetics on either the viscosity of the medium or the ET driving force. Comparisons to directly measured ground-state folding thermodynamic parameters (if they can be obtained) would also be illuminating.

(15) An additional incentive conceivably could be diminution of the separation-distance-dependent solvent reorganization energy (see, for example, ref 1a).

(16) Yoon, D. I.; unpublished work.

Specific Molecular Recognition via Multipoint Hydrogen Bonding Ubiquinone Analogues—Porphyrin Having Four Convergent Hydroxyl Groups Pairing

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Interaction between quinone and porphyrin is of current interest in the study of electron transfer in photosynthesis and the respiratory chain.[1,2] The noncovalent interaction of ubiquinone at the both redox sites of enzymes seems to be especially important in respiratory electron transfer via molecular recognition.[3,4]

* Authors to whom correspondence should be addressed.

(1) Deisenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. *J. Mol. Biol.* **1984**, *180*, 385.

(2) Gennis, R. B. *Biomembranes*; Springer-Verlag: New York, 1989.

(3) (a) Crane, F. L. *Annu. Rev. Biochem.* **1977**, *46*, 439. (b) Hackenbrock, C. R.; Chazotte, B.; Gupte, S. S. *J. Bioenerg. Biomembr.* **1986**, *18*, 331. (c) Lenaz, G.; Fato, R. *J. Bioenerg. Biomembr.* **1986**, *18*, 369.

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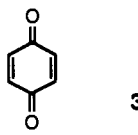
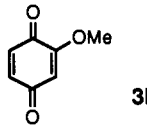
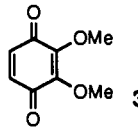
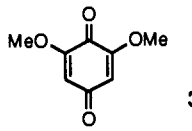
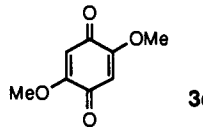
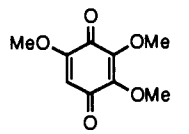
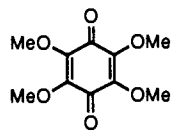
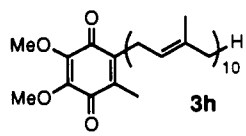
Table I. Binding Constants (K_a) and Thermodynamic Parameters for Porphyrin **1**–Quinone **3** Complexation in $CHCl_3$ at 298 K[a]

quinone	K_a (M^{-1})[b]	$\Delta G°$ (kcal/mol)	$\Delta H°$ (kcal/mol)[c]	$T\Delta S°$ (kcal/mol)[d]
 **3a**	3.0 × 10	−2.0	−6.5	−4.5
 **3b**	7.4 × 10	−2.5	−6.8	−4.2
 **3c**	8.3×10^2	−4.0	−7.8	−3.8
 **3d**	1.7×10^2	−3.0	−6.0	−3.0
 **3e**	1.9×10^2	−3.1	−5.9	−2.8
 **3f**	1.6×10^3	−4.4	−9.0	−4.7
 **3g**	2.0×10^4	−5.8	−10.5	−4.7
 **3h**	1.6×10^2	−2.9	−5.5	−2.5

[a] Binding constants and thermodynamic parameters were determined by visible titration at 584 nm. [b] Errors in K_a are <4%. [c] Errors in $\Delta H°$ are <7%. [d] Errors in $\Delta S°$ are <14%.

Investigations on noncovalent porphyrin–quinone aggregates are, however, very few.[5] Recently, we reported the intermolecular interaction between various quinones and porphyrin via two-point hydrogen bondings as a model system, although this porphyrin did not show enough affinity for ubiquinone analogues.[6] In this communication, we describe the modes of hydrogen-bonded complexation of various ubiquinone analogues with the particular receptor *meso*-tetra($\alpha,\alpha,\alpha,\alpha$-2-hydroxy-1-naphthyl)porphyrin (**1**) via the two types of hydrogen bonding.

Condensation of 2-methoxy-1-naphthaldehyde and pyrrole followed by demethylation of the product *meso*-tetra(2-methoxy-1-naphthyl)porphyrin with BBr_3 led to a satisfactory yield of *meso*-tetra(2-hydroxy-1-naphthyl)porphyrin.[7] Four atropisomers of obtained porphyrin were easily separated by silica gel chromatography to give the $\alpha,\alpha,\alpha,\alpha$-atropisomer.[8] No atropisomerization of **1** was detected after the product was boiled in toluene for 2 h. Porphyrin **1**, having four convergent hydroxyl groups, can specifically bind with ubiquinone analogues **3b–g** at 1:1 stoichiometry. Face-to-face complexation between **1** and **3** was confirmed by the downfield shift of the hydrogen-bonding OH of **1** and upfield shifts of the OCH_3 and ring protons of quinone due to ring current of the porphyrin macrocycle in the

Table II. Comparison of Binding Constants between **1** and **2** at 298 K (M^{-1})

host	quinone **3a**	quinone **3g**	quinone **3i**
1 (tetra-OH)[a]	3.0 × 10	2.0×10^4	2.8×10
2 (di-OH)[b,c]	5.5 × 10	7.8	4.2×10^2

[a] In $CHCl_3$. [b] Host **2** is 5,15-*cis*-bis-(2-hydroxy-1-naphthyl)octaethylporphyrin (ref 6). [c] In $CDCl_3$.

(4) Robinson, H. H.; Kahn, S. D. *J. Am. Chem. Soc.* **1990**, *112*, 4728.
(5) (a) Tecilla, P.; Dixon, R. P.; Slobodkin, G.; Alavi, D. S.; Waldeck, D. H.; Hamilton, A. D. *J. Am. Chem. Soc.* **1990**, *112*, 9408. (b) Harriman, A.; Magda, D. J.; Sessler, J. L. *J. Chem. Soc., Chem. Commun.* **1991**, 345. (c) Harriman, A.; Magda, D. J.; Sessler, J. L. *J. Phys. Chem.* **1991**, *95*, 1530. (d) Harriman, A.; Kubo, Y.; Sessler, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 388. (e) Turrō, C.; Chang, C. K.; Leroi, G. E.; Cukier, R. I.; Nocera, D. G. *J. Am. Chem. Soc.* **1992**, *114*, 4013.
(6) Aoyama, Y.; Asakawa, M.; Matsui, Y.; Ogoshi, H. *J. Am. Chem. Soc.* **1991**, *113*, 6233.
(7) Yields for the porphyrin synthesis and following demethylation step are 6.2% and >99%, respectively. Column chromatography separation of four atropisomers afforded the $\alpha,\alpha,\alpha,\alpha$-atropisomer **1** in 11% yield.
(8) Host **1** was characterized by ^1H and ^{13}C NMR and HRMS.

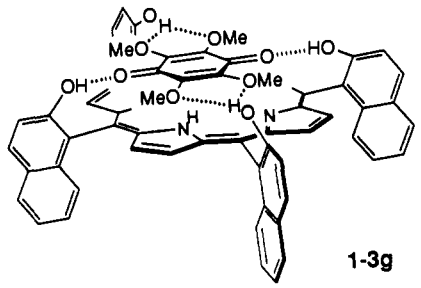


Figure 1. Schematic representation of **1**–**3g** complexation.

^{1}H NMR spectrum.[9] These affinities were determined by titrimetric measurement of visible spectra with clear isosbestic points in the region of 550–700 nm.

The binding constants calculated from the nonlinear curve fitting analysis and thermodynamic parameters for porphyrin **1**–quinone **3** complexation are summarized in Table I. Significant binding properties are as follows. The binding constants of quinones with **1** unambiguously increase in the order **3a** < **3b** < **3c** < **3f** < **3g** with the number of OCH_3 groups. The favorable negative changes of free energy and enthalpy increase in the same order as above. The trend of complexation is not predictable from the entropy changes for **3a**–**c**, **3f**, and **3g**. The positions of methoxy groups are crucial in the host–guest formation. In general, the negative gain of free energy change of the methoxy substitutions at the adjacent positions (−1.3 to approximately −1.5 kcal/mol) is about three times larger than that of substitutions at the separate positions. The remarkable enhancement of the binding constant of 2,3-dimethoxy-*p*-benzoquinone (**3c**) compared with 2,6- and 2,5-dimethoxy-*p*-benzoquinones (**3d**,**e**) implies that two adjacent OCH_3 substituents at 2- and 3-positions of the *p*-benzoquinone ring cooperatively act as the effective third interaction site via *bifurcated* hydrogen bonding. In contrast, the effective third and/or fourth point interactions between **3d** or **3e** and **1** seem to be much weaker than those in the former case. Simultaneous *multipoint* hydrogen bondings give rise to an extremely large binding constant for tetramethoxy-*p*-benzoquinone (**3g**) with **1** (Figure 1). It should be noted that ubiquinone (**3h**), having a long isoprenoid tail, has an appreciably high affinity with **1**.

Furthermore, it is of particular interest to compare the affinities of quinones for **1** and the previous host 5,15-*cis*-bis-(2-hydroxy-1-naphthyl)octaethylporphyrin (**2**), substituted with two hydroxynaphthyl groups at meso-positions and eight peripheral ethyl groups at β-positions. The sharp difference in binding properties between **1** and **2** is shown in Table II. In spite of no substantial difference in binding constants for **3a**, complexation of **3g** with **1** is ca. 250 times larger than that with **2**, although methoxy groups may bring about steric hindrance to 2-hydroxynaphthyl groups and a weakening charge-transfer-type interaction. It is likely that the very low binding constant for pairing of **2** and **3g** results from steric hindrance between ethyl groups of **2** and methoxy groups of **3g**. Pairing of tetramethyl-*p*-benzoquinone (**3i**) with **1** shows a marked decrease in the binding constant due to a repulsive interaction between methyl groups and 2-hydroxynaphthyl groups. The fashion of the present quinone–porphyrin **1** pairing is quite different from the system of two-point hydrogen-bonding fixation which is governed by both an electronic effect of the substituents and a charge-transfer-type interaction.[6]

Further work on the structural properties of quinone–porphyrin adducts and the kinetics of electron transfer from a photoexcited porphyrin to quinone are in progress, and details on these will appear in future publications.

Acknowledgment. This work was supported by a Grant-in-Aid for Specially Promoted Research (No. 04101003) from the Ministry of Education, Science, and Culture, Japan.

(9) For example, the following values of $\Delta\delta$, δ (**1** + **3g**) − δ(**1** or **3g**), are observed under the conditions [**1**] = [**3g**] = 2.0 mM in $CDCl_3$ at 30 °C: +1.91 (OH of **1**), −0.93 (CH_3 of **3g**).

Metal-Mediated Dimerization of 1,3-Cyclooctadiene to 2-Cyclooct-2-en-1-yl-1,3-cyclooctadiene: A Novel Bicyclic Triene[1]

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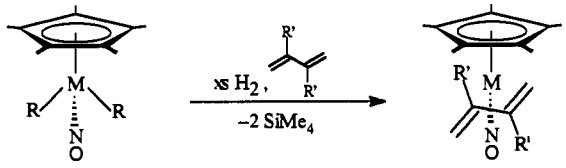
We have previously reported the synthesis and characteristic reactivity of unusual Cp′Mo(NO)(η^4-*trans*-diene) complexes [Cp′ = Cp (η^5-C_5H_5) or Cp* (η^5-C_5Me_5)].[2] These complexes are preparable via sodium amalgam reduction in THF of Cp′Mo(NO)I_2 in the presence of acyclic, conjugated dienes. However, this reduction method cannot be extended to encompass cyclic, conjugated dienes.[2a] Furthermore, similar reductions of Cp′W(NO)I_2 in THF in the presence of cyclic or acyclic conjugated dienes simply result in decomposition of the organometallic reactant.[2a] We now report a new method for the synthesis of Cp*M(NO)(η^4-*trans*-diene) complexes of *both* molybdenum and tungsten. This method involves treating solutions of Cp*M(NO)(CH_2SiMe_3)$_2$ [M = Mo, W] with H_2 in the presence of acyclic, conjugated dienes (eq 1).[3]



(1)

However, when 1,3-cyclooctadiene (1,3-COD) is employed as the trapping agent, it undergoes an unprecedented coupling in the metals' coordination spheres (Scheme I). The 2-cyclooct-2-en-1-yl-1,3-cyclooctadiene ligand thus formed is attached in a bis-η^2 fashion to the metal centers in the final products.[3] This hitherto unknown triene is easily liberated by treatment of these complexes with O_2.[4]

Typically, the Cp*M(NO)(CH_2SiMe_3)$_2$ reactants were exposed to an excess of diene and H_2 (1 atm) at −78 °C in Et_2O for 1 h (M = Mo) or 16 h (M = W). Chromatographic separation of the final reaction mixtures on Florisil and subsequent workup afforded yellow crystals of the various product complexes.[3] The spectroscopic properties of the new Cp*W(NO)(η^4-*trans*-diene) complexes resemble those exhibited by related molybdenum species whose molecular structures we have previously established.[2] Hence, it is likely that both of these compounds are isostructural and contain the diene ligands attached to the metal centers in a twisted, transoidal fashion.[2,6] In contrast, the spectroscopic properties of the organometallic products resulting from the re-

(1) Presented in part at the 75th Canadian Chemical Conference, Edmonton, Alberta, Canada, June 1992; Abstract 370.

(2) (a) Christensen, N. J.; Hunter, A. D.; Legzdins, P. *Organometallics* **1989**, *8*, 930. (b) Christensen, N. J.; Legzdins, P.; Einstein, F. W. B.; Jones, R. H. *Organometallics* **1991**, *10*, 3070. (c) Christensen, N. J.; Legzdins, P.; Trotter, J.; Yee, V. C. *Organometallics* **1991**, *10*, 4021. (d) Christensen, N. J. Ph.D. Dissertation, The University of British Columbia, 1990.

(3) Complete experimental details and characterization data for all complexes isolated during this work are provided as supplementary material.

(4) The organometallic product of this transformation is the well-known [Cp*M$(O)_2]_2(\mu$-O).[5] Interestingly, both Cp*M(NO)($C_{16}H_{24}$) complexes are stable to reducing conditions (e.g., Na/Hg amalgam) and do not react to any appreciable extent with CO (600 psig, 5 days) at room temperature.

(5) Faller, J. W.; Ma, Y. *J. Organomet. Chem.* **1988**, *340*, 59.

(6) (a) Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1. (b) Yasuda, H.; Tatsumi, K.; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120.

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