by $^1H$ NMR in the presence of Eu(hfc)$_3$) having the identical physical data with those of the authentic sample: $[\alpha]^{23}_D$ 87.4° (c 1.0, $CHCl_3$) ($[\alpha]^{23}_D$ (c 1.0, $CHCl_3$) of the authentic sample was 90.9°); mp 91.6–93.3 °C (mp of the authentic sample was 92.0–94.6 °C); $^1H$ NMR ($CDCl_3$) δ 1.09 (t, J = 7.33 Hz, 3 H), 1.83 (s, 3 H), 2.97 (m, 2 H), 4.02 (q, J = 7.33 Hz, 2 H), 4.73 (q-like, J = 6.59 Hz, 1 H), 6.71 (d, J = 7.69 Hz, 1 H), 7.0–7.2 (m, 5 H); $^{13}C$ NMR ($CDCl_3$) δ 13.6, 22.4, 37.4, 53.0, 60.9, 126.5, 128.0, 128.8, 135.8, 169.6, 171.5.

**Large-Scale Preparation of Methyl 7-(Tetrahydropyranyloxy)-5-heptynoate from 7-(Tetrahydropyranyloxy)-5-heptynoic Acid and Methyl Iodide.** A mixture of 7-(tetrahydropyranyloxy)-5-heptynoic acid (6.0 g, 26.4 mmol), CsF (8.8 g, 58 mmol), MeI (8.2 g, 58 mmol), and DMF (100 mL) was stirred at 30 °C for 18 h. The reaction mixture was extracted with EtOAc and washed with saturated aqueous $NaHCO_3$ (100 mL × 3). The organic layer was dried ($Na_2SO_4$) and evaporated to give an oil. Column chromatography on silica gel (95:5 hexane–EtOAc) of this oil provided methyl 7-(tetrahydropyranyloxy)-5-heptynoate (5.0 g, 79%) having spectral data identical with those of the authentic sample.[8]

**General Procedure for the Preparation of Esters from Tributyltin Carboxylates and Alkyl Halides in the Presence of Cesium Fluoride.** A mixture of hexabutyldistannoxane (656 mg, 1.1 mmol), (*S*)-*N*-acetylphenylalanine (414 mg, 2 mmol), and benzene (30 mL) was heated under refluxed in a Dean-Stark apparatus for 3 h. The benzene was removed under reduced pressure, and DMF (6 mL) was added. To this solution were added CsF (456 mg, 3 mmol) and EtI (468 mg, 3 mmol), and the reaction mixture was stirred at 30 °C for 30 h. Aqueous workup as described for reaction of (*S*)-*N*-acetylphenylalanine with ethyl iodide and column chromatography on silica gel (50:50 benzene–EtOAc) afforded ethyl (*S*)-*N*-acetylphenylalanine (430 mg, 91%, ≥98% ee determined by $^1H$ NMR in the presence of Eu(hfc)$_3$): $[\alpha]^{23}_D$ 88.0° (c 1.0, $CHCl_3$); mp 92.0–94.0 °C. The product was identical in all respects with the authentic sample.

**Reaction of Tributyltin Benzoate with Ethyl Iodide. A. In the Presence of Cesium Fluoride.** A mixture of tributyltin benzoate (411 mg, 1 mmol), EtI (234 mg, 1.5 mmol), CsF (228 mg, 1.5 mmol), and DMF (3 mL) was stirred at 30 °C for 2.5 h. Usual workup gave an oil. GLC analysis of this oil revealed the formation of ethyl benzoate in 95% yield.

**B. In the Absence of Cesium Fluoride.** A mixture of tributyltin benzoate (411 mg, 1 mmol), EtI (234 mg, 1.5 mmol), and DMF (3 mL) was stirred at 30 °C for 19 h. No ethyl benzoate could be detected by GLC analysis.

**Registry No.** CsF, 13400-13-0; KF, 7789-23-3; benzoic acid, 65-85-0; dodecanoic acid, 143-07-7; cyclohexanecarboxylic acid, 98-89-5; phthalic acid, 88-99-3; triphenylacetic acid, 595-91-5; 2,4,6-trimethylbenzoic acid, 480-63-7; (*E*)-2-hexenoic acid, 13419-69-7; (*E*)-3-hexenoic acid, 1577-18-0; 2-octynoic acid, 5663-96-7; *N*-acetylphenylalanine, 2018-61-3; (*S*)-2-hydroxypropanoic acid, 79-33-4; (*R*)-α-hydroxycyclohexaneacetic acid, 53585-93-6; (*S*)-α-hydroxycyclohexaneacetic acid, 61475-31-8; (*S*)-α-ethylbenzeneacetic acid, 4286-15-1; ethyl benzoate, 93-89-0; allyl benzoate, 583-04-0; benzyl benzoate, 120-51-4; isopropyl benzoate, 939-48-0; *tert*-butyl benzoate, 774-65-2; ethyl dodecanoate, 106-33-2; ethyl cyclohexanecarboxylate, 3289-28-9; butyl phthalate, 84-74-2; ethyl triphenylacetate, 5467-22-1; ethyl 2,4,6-trimethylbenzoate, 1754-55-8; methyl (*E*)-2-hexenoate, 13894-63-8; methyl (*E*)-3-hexenoate, 13898-61-8; methyl 2-octynoate, 111-12-6; ethyl (*S*)-2-hydroxypropanoate, 687-47-8; methyl (*R*)-α-hydroxycyclohexaneacetate, 92587-21-8; methyl (*S*)-α-hydroxycyclohexaneacetate, 121099-13-6; ethyl *N*-acetylphenylalanine, 2361-96-8; methyl 12-(tetrahydropyranyloxy)octadecanoate, 138982-91-9; ethyl cyanoacetate, 105-56-6; methyl 12-(*tert*-butyldimethylsiloxy)dodecanoate, 95841-29-5; ethyl 2-benzoxybenzoate, 604-61-5; methyl 2-acetoxybenzoate, 580-02-9; methyl 4-acetoxybenzoate, 24262-66-6; diethyl phthalate, 84-66-2; 12-(tetrahydroxypyranyloxy)octadecanoic acid, 79967-16-1; cyanoacetic acid, 372-09-8; 12-(*tert*-butyldimethylsiloxy)dodecanoic acid, 77744-42-4; 2-benzoylbenzoic acid, 85-52-9; 2-acetoxybenzoic acid, 50-78-2; 4-acetoxybenzoic acid, 2345-34-8; ethyl iodide, 75-03-6; ethyl methanesulfonate, 62-50-0; ethyl bromide, 74-96-4; allyl bromide, 106-95-6; benzyl bromide, 100-39-0; isopropyl iodide, 75-30-9; *tert*-butyl iodide, 588-17-0; 1-iodo-2,2-dimethylpropane, 15501-33-4; butyl iodide, 542-69-8; methyl iodide, 74-88-4; 12-hydroxydodecanoic acid, 505-95-3; 12-hydroxyoctadecanoic acid, 106-14-9; methyl (*S*)-α-ethylbenzeneacetate, 26164-15-8; 7-(tetrahydropyranyloxy)-5-heptynoic acid, 34506-49-5; methyl 7-(tetrahydropyranyloxy)-5-heptynoate, 50781-90-3; cinnamic acid, 621-82-9; *N*-acetylvaline, 96-81-1; ethyl cinnamate, 103-36-6; ethyl *N*-acetylvaline, 2382-78-7; hexabutyldistannoxane, 56-35-9; tributyltin benzoate, 4342-36-3.

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# Design, Synthesis, and Characterization of a "Shopping Basket" Bis-porphyrin. The First Examples of Triply Bridged Closely Interspaced Cofacial Porphyrin Dimers

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The biscobalt complexes of quadruply bridged closely interspaced 5,10,15,20-tetraphenylporphyrin dimers have proven to be effective catalysts for the 4e$^-$ reduction of $O_2$ to water when adsorbed onto the disk of a rotating ring–disk electrode or when dissolved in aqueous acidic medium.[1,2] From electrochemical and NMR data, we find a linear relationship between the interplanar distance in the porphyrin dimer and the percentage of $O_2$ reduced by the 4e$^-$ reduction pathway.[1]

By use of molecular dynamics, we find that the triply bridged porphyrin dimer **1a**, as compared to a comparable quadruply bridged porphyrin **2** is more flexible and can reach a shorter interplanar distance. Following the CHARM$_m$ modeling design, we have synthesized the first triply bridged porphyrin dimer **1a** and we have chosen to name it a "shopping basket" bis-porphyrin. The R group in **1a** was chosen to be *m*-pyridinesulfonamide because this group proved to effect the smallest possible interplanar distances in the limited family of quadruply bridged dimers that we have studied. In addition, **1a** is a convenient precursor to a water-soluble dimer.

Following Lindsey's method,[3] Lewis acid catalyzed ($BF_3$·$Et_2O$) high dilution condensation of 3 equiv of α-bromo-*m*-tolualdehyde[1] and 1 equiv of *m*-tolualdehyde with pyrrole (chloroform, room temperature) followed by in situ tetrachloro-1,4-benzoquinone oxidation of the intermediate porphyrinogen (chloroform, 60 °C) and separation by chromatography on silica gel using ethyl acetate/hexane (1:10) as eluent afforded the parent monom-

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(2) Collman and co-workers were the first to conceive and practice the idea of effecting four-electron reduction of $O_2$ to $H_2O$ using face-to-face porphyrins. For further information see: (a) Collman, J. P.; Marrocco, M.; Denisevich, P.; Koval, C.; Anson, F. C. *J. Electroanal. Chem.* **1979**, *101*, 117. (b) Collman, J. P.; Denisevich, P.; Konai, Y.; Marrocco, M.; Koval, C.; Anson, F. C. *J. Am. Chem. Soc.* **1980**, *102*, 6027. (c) Collman, J. P.; Hendricks, N. H.; Leidner, C. R.; Ngameni, E.; L'Her, M. *Inorg. Chem.* **1988**, *27*, 387. (d) Durand, R. R., Jr.; Bencosme, C. S.; Collman, J. P.; Anson, F. C. *Ibid.* **1983**, *105*, 2710. (e) Collman, J. P.; Anson, F. C.; Bencosme, S.; Chong, A.; Collins, T.; Denisevich, P.; Evitt, E.; Geiger, T.; Ibers, J. A.; Jameson, G.; Konai, Y.; Koval, C.; Meier, K.; Okaley, P.; Pettman, R.; Schmittou, E.; Sessler, J. In *Organic Synthesis Today and Tomorrow*, Trost, B. M., Hutchinson, C. R., Eds.; Pergamon Press: Oxford, 1981; pp 29–45.

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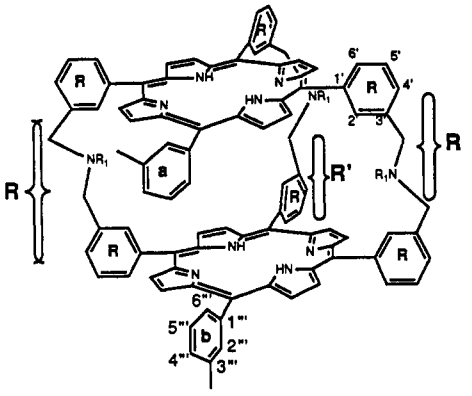
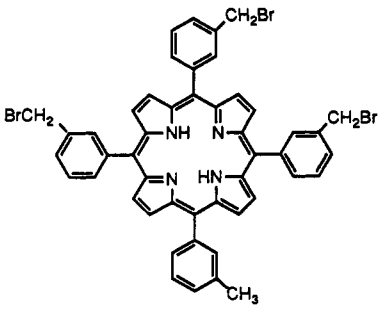


1a $R_1$ = —$SO_2$—

eric porphyrin **3**, in 12% yield.

Self-assembly procedure[1] involving base-mediated ($Cs_2CO_3$) high dilution coupling of 2 equiv of **3** with 3 equiv



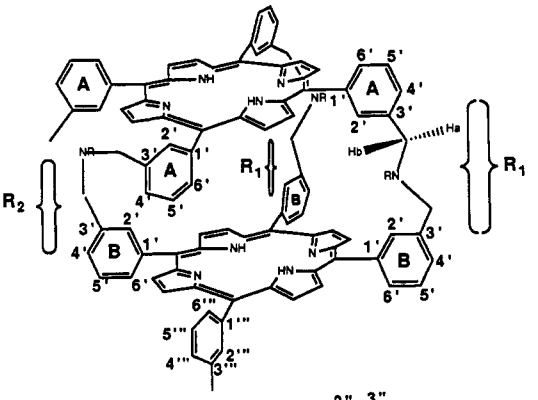
**3**

of pyridinesulfonamide[1c,4] in DMF and isolation by chromatography on silica gel using chloroform as an eluent provided the first triply bridged closely interspaced porphyrin dimer **1a** along with its less polar isomer **1b** in 7% and 3% yields, respectively. The assigned structure **1b** represents a "mismatch" in the self-assembly process where two adjacent benzyl bromides on **3** are coupled via two *m*-pyridinesulfonamides to two transoid benzyl bromides.

The porphyrin dimers **1a** and **1b** were characterized by 2D $^1H$–$^1H$ and 2D $^1H$–$^{13}C$ NMR (DQF-COSY), UV/vis, fluorescence, and FABMS. The 2D $^1H$–$^{13}C$ NMR of **1a** is shown in Figure 1. The $^1H$-NMR, UV/vis, and fluorescence spectra of dimers **1a** and **1b** are quite different from the corresponding monomeric porphyrin **3**. In the $^1H$-NMR, the pyrrolic NH protons of **1a** and **1b** are more shielded than that of the monomer **3** ($\delta$ −3.92 for **1a**, −3.32 for **1b** vs −2.69 ppm for **3**). UV/vis spectra of **1a** and **1b** show broadened, blue-shifted Soret bands compared to **3** (see Table I). The intensities of the emission band in the fluorescence spectra of the dimers **1a** and **1b** are greatly quenched comparing to that of **3** (see Table I). FABMS of the two isomers **1a** and **1b** show a molecular peak (M + 1) at 1803.5 ([$M^+$] = $C_{111}H_{83}N_{14}O_6S_3$).

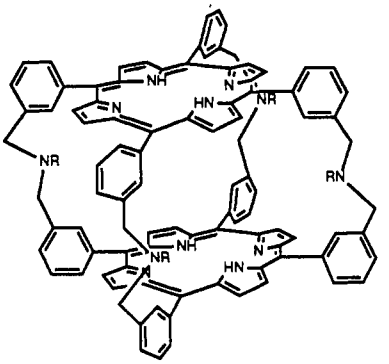
The physical properties of dimers **1a** and **1b** differ from monomer **3** because of the existence of $\pi$–$\pi$ interactions in the dimers.[1] Similarly, the differences in the $^1H$-NMR, UV/vis, and fluorescence spectra of the two dimeric isomers **1a** and **1b** stem from the difference in the interplanar distances in the dimers. In dimer **1a** the interplanar distance is shorter than in **1b**, and as a result the $\pi$–$\pi$ interactions between the two porphyrin cores in **1a** are greater than in **1b**.

(4) See: (a) Franklin, J. *Inst.* **1943**, *236*, 316–320; *Chem. Abstr.* **1943**, *37*, 6652. (b) Machek, G. *Monatsh* **1938**, *72*, 77–92; *Chem. Abstr.* **1938**, *32*, 9087 and ref 1b–c.



**1b** R = —$SO_2$—

The gas-phase global minimum structure of **1a** (Figure 2) was obtained by use of $CHARM_m$ molecular dynamics calculations to 110 ps.[5] From Figure 2 the porphyrin cores of **1a** are coplanar, the interplanar distance (P–P) is 5.22 Å, and center to center distance (Ct–Ct) is 5.57 Å. From 2000 conformations sampled during 100-ps collection phase in molecular dynamics the distance Ct–Ct in dimer **1a** varies from 4.5 to 7.1 Å (see trace a in Figure 3), while for the quadruply bridged dimer **2** the range is 4.8 to 6.4 Å. The distribution of energies as a function of the interplanar distances are shown as trace b in Figure 3. The calculated properties shown in Figure 3 indicate that dimer **1a** displays increased flexibility compared to **2**.



**2** R = —$SO_2$—

The $CHARM_m$ calculated global minimum structure of **1b** is forced to quite open and tilted, and P–P and Ct–Ct were found to be 6.30 and 6.54, respectively. The conformational flexibility of **1b** is shown as traces c and d in Figure 3. It is evident from Figure 3c that the range of distances covered during 100 ps of dynamics at 600 K is 5.0–10.2 Å, which is quite wide compared with **1a**. The distribution plot in Figure 3d shows that the values for Ct–Ct concentrate between 5.5 and 8.0 Å and the observed minimum structure **1b** falls in the middle of this range.

To further support the conformational flexibility calculated by $CHARM_m$, the $^{13}C$ relaxation times ($^{13}C$ $T_1$) as a measure of the segmental motion of the porphyrin molecules **1a** and **2** have been evaluated.[6] $T_1$ is typically

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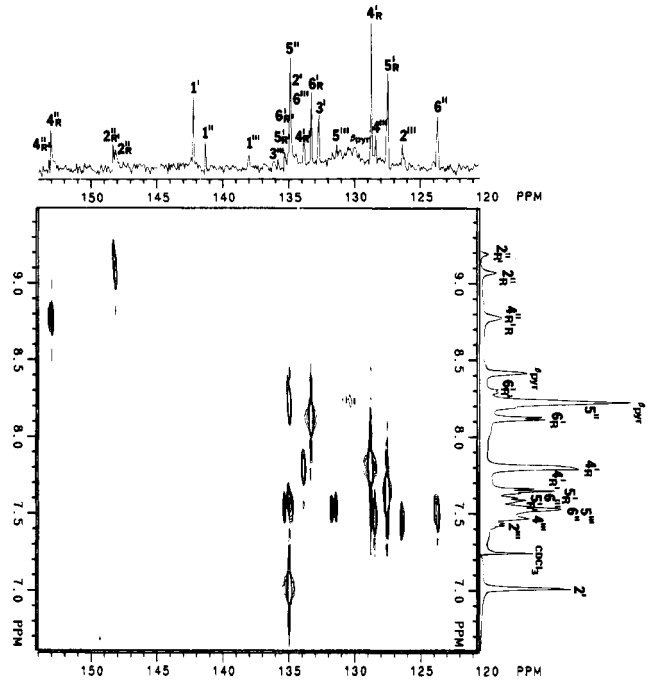

**Figure 1.** 2-D $^{13}C$–$^{1}H$ NMR for dimer **1a** in $CDCl_3$ (aromatic region).

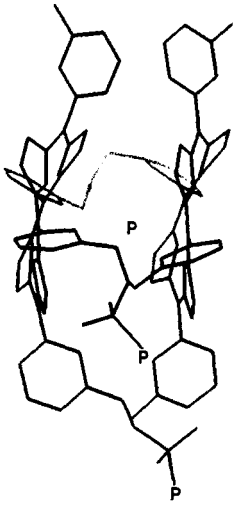

**Figure 2.** CHARMm global minimum for "shopping basket" porphyrin dimer **1a**. Sidechain P (*m*-pyridyl) is omitted for clarity.

**Table I. UV/vis and Emission Spectra of 1a, 1b, and 3 in $CHCl_3$**

| compd | Soret band width at half peak height (nm) | UV/vis $\lambda_{max}$(nm) ($\epsilon \times 10^{-3}$ $cm^{-1}$ $M^{-1}$) | emission at $\lambda$ 650.1 rel intens |
|---|---|---|---|
| **1a** | 18 | 406 (307, sh), 414 (472), 515 (21.3), 550 (8.1), 590 (5.8), 648 (3.2) | 0.17 |
| **1b** | 13 | 408 (297, sh), 416 (551), 516 (24.3), 552 (8.7), 591 (6.6), 647 (3.4) | 0.52 |
| **3** | 12 | 419 (397), 515 (15.6), 551 (6.1), 591 (4.0), 647 (2.3) | 1.0 |

dominated by dipole–dipole interactions and can be related to an average correlation time, $\tau_c$.[6] For a molecule rotating isotropically with internal motions, $\tau_c$ is given by eq 1,

$$1/\tau_c = 1/\tau_r + 1/\tau_g \quad (1)$$

where $\tau_r$ is a correlation time for the overall reorientation of the molecule and $\tau_g$ is an effective correlation time for internal motions. For large-size molecules the overall reorientation becomes slower and the $\tau_g$ dominates $\tau_c$.[6] In agreement with this concept, we can compare the mobility of two different porphyrins by measuring the $^{13}C$ $T_1$ of the benzylic carbons ($CH_2$) of the porphyrin. For the quadruply bridged dimer **2** the $T_1$ relaxation time of the $CH_{2's}$ is very small (0.1 s) which denotes a very rigid structure. While in the triply bridged dimer **1a** the $T_1$ relaxation time of the benzylic carbons ($CH_2$) is larger by factor of 4 (0.4 s). This result is in perfect agreement with $CHARM_m$ molecular dynamics calculations (vide supra).

## Experimental Section

**General.** General nuclear magnetic resonance spectra were obtained on a General Electric GN-500 spectrophotometer at 25 °C. Chemical shifts in ppm were referenced to $CHCl_3$ ($^{1}H$, 7.240 ppm; $^{13}C$, 77.000 ppm). Phase-sensitive double quantum filtered COSY spectra were recorded using a pulse sequence[7] 90°–$t_1$–90°$_{\Phi1}$–Δ–90°$_{\Phi2}$–aquisition$_{\Phi R}$ with 90° pulse of 22.5 μs calibrated before the experiment, Δ = 8 μs, and an eight-step phase cycling has been applied.[8,9] Spectra were collected into 4K data blocks for 256 $t_1$ increments with a relaxation delay of 1.5 s. Spectral width in both dimensions was 7100 Hz for **1b**. The data matrix was zero filled to 2K and apodized with exponential function to give a line broadening of 1 Hz in both dimensions. 2D $^{13}C$–$^{1}H$ heteronuclear shift correlation data were recorded using a pulse sequence[10] $^{1}H$, 90°$_{\Phi1}$–$t_1$–$\Delta_1$–90°$_{\Phi2}$–$t$–$\Delta_2$–decouple; $^{13}C$, $t_{1/2}$–180°$_{\Phi1}$–$t_{1/2}$–$\Delta_1$–$t$–90°$_{\Phi3}$–$\Delta_2$–aquisition$_{\Phi R}$ with a 90° ($^{13}C$) pulse of 17.5 μs, 90° ($^{1}H$) pulse of 32 μs calibrated before the experiment, and with an eight-step phase cycling to afford quadrature detection in both frequency domains. Spectra were collected into 4K data blocks for 130 $t_1$ increments with a relaxation delay of 1.5 s, $\Delta_1$ = 3.2 ms, $\Delta_2$ = 2.1 ms, $\tau$ = 10 μs. Spectral width in the first dimension was 8333.33 Hz and 15151.50 Hz in the second dimension. Data matrix were zero filled to 1K and apodized with double exponential function to give a line broadening of 3 Hz in both dimensions. Relaxation times $T_1$ were measured at 125.76 MHz with a GN-500 NMR spectrometer by using an inversion–recovery method.[11] Alternate 90° pulses were shifted by 180° relative to the inversion pulses to optimize the response. To allow for this shift, the phase of the receiver was shifted 180° on alternate scans. A composite 180° pulse was used to compensate for imperfect magnetic field homogeneity and off-resonance field strength fall off. The relaxation delay was 7 s, and the longest variable delay pulse was also 7 s. The $T_1$ values were calculated by using a nonlinear fit of the three-parameter equation of Levy[12] for fast inversion–recovery fourier transform (FT) experiments. All relaxations were measured at 25 °C unless specified. Absorption spectra were recorded on a Cary-14 spectrophotometer interfaced to a Zenith computer equipped with OLIS (On-Line Instrument System Inc.) data acquisition and processing software. Fast atom bombardment (FAB) mass spectroscopy was performed at UCSB using *m*-nitrobenzyl alcohol as the matrix and a parallel run of cesium rubidium iodide as the reference. Emission spectra were run on Perkin-Elmer LS 50. Melting points were taken on Laboratory Devices MEL-TEMP apparatus and are uncorrected. α-Bromo-*m*-tolunitrile, pyrrole, diisobutylaluminum hydride (DIBAL-H), phosphorus oxychloride, phosphorus pentachloride, *m*-tolualdehyde, cesium carbonate, and 3-pyridinesulfonic acid were purchased from Aldrich. All other reagents were commercially obtained in high purity. All reactions were carried out with purified reagents in dry, purified solvents under argon unless noted otherwise. Column chromatography was performed with

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(9) Morris, G. A. *Magn. Reson. Chem.* **1980**, *24*, 371.
(10) See ref 7, p 178.
(11) (a) Cutnell, J. D.; Bleich, H. E.; Glasel, J. A. *J. Magn. Reson.* **1976**, *21*, 43. (b) Freeman, R.; Kempsell, S. P.; Levitt, M. H. *J. Magn. Reson.* **1980**, *38*, 453.
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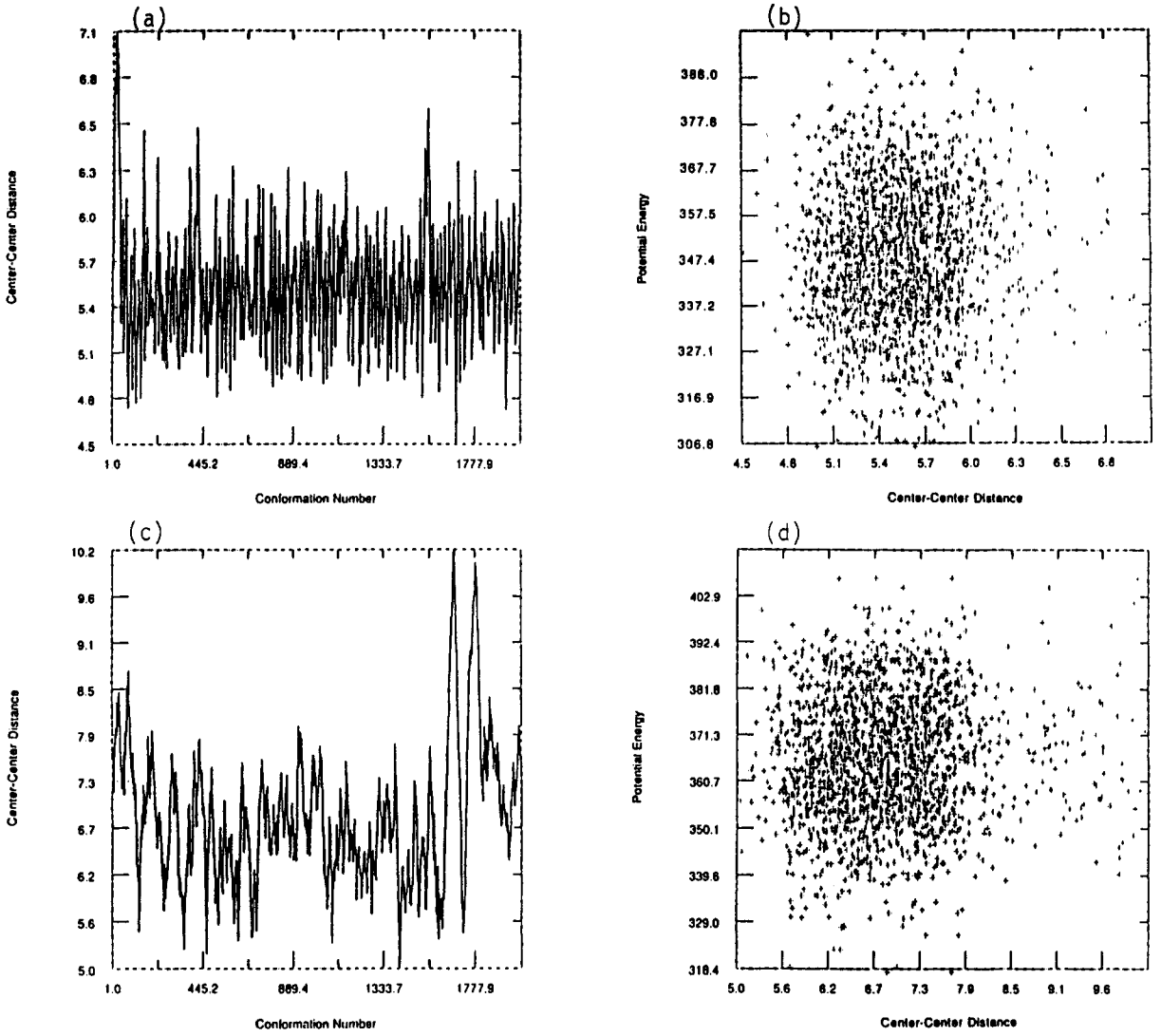


**Figure 3.** Key: (a) Center–center distance between porphyrin planes in dimer **1a** as a function of dynamics trajectory, (b) potential energy distribution for **1a** as a function of center–center distance between porphyrin planes, (c) center–center distance between porphyrin planes in dimer **1b** as a function of dynamics trajectory, and (d) potential energy distribution for **1b** as a function of center–center distance between porphyrin planes.

Fischer-type 60-Å (200–425 mesh) silica gel. Preparative thin-layer chromatography (TLC) was performed using E.M. Sciences Kieselgel 60 $F_{254}$. Reversed-phase preparative thin-layer chromatography (TLC) was performed using Whatman PLKC18F glass-backed plates.

**Theoretical Calculations.** All model building and calculations were performed on a Silicon Graphics IRIS 4D/220 GTX workstation, using the programs Quanta Version 3.2 (Polygen Corp) and $CHARM_m$[5] Version 21.2. The topology file PORPHYRINH.RTF supplied by Polygen was used as a basis for the porphyrin moieties of the dimers and the linkers were constructed in Chemnote, the 2D modeling facility in Quanta. Minimizations were performed using steepest descent algorithm, followed by adopted basis Newton–Raphson algorithm, until the energy change tolerance was less than $10^{-9}$ kcal/mol. Nonbonded interaction cutoff distance and hydrogen bonding cutoff distance were chosen to be 11.5 and 7.5 Å, respectively. Molecular dynamics were performed using Verlet integration and the SHAKE algorithm to fix C–H bonds. At 600 K, the maximum allowable fluctuation in temperature was fixed at 25 °C. Nonbonded interaction and hydrogen bond lists were updated every 0.001 ps. A stepsize of 0.001 ps/step was used, and conformational sampling was done every 50 steps (0.05 ps).

**α-Bromo-*m*-tolualdehyde** was prepared as previously reported:[1a,1c] white crystals, mp 46 °C (lit.[1a] mp 45–46 °C); IR (KBr) 1595, 1610 (m, C=C), 1710 (s, C=O); $^1$H-NMR ($CDCl_3$) δ 4.54 (s, 2 H, $CH_2Br$), 7.51 (t, 1 H, $J$ = 8 Hz), 7.66 (d, 1 H, $J$ = 8 Hz), 7.82 (dt, 1 H, $J$ = 8,1 Hz), 7.90 (s, 1 H), 10.02 (s, 1 H, CHO); $^{13}$C-NMR ($CDCl_3$) δ 32.0 ($CH_2Br$), 129.6, 129.7, 129.8, 134.8, 136.8, 138.9, 191.6 (CHO).

**5,10,15-Tris(α-bromo-*m*-tolyl)-20-*m*-tolylporphyrin, 3.** Boron trifluoride etherate (1.33 mL, 11 mmol) was added to a solution containing α-bromo-*m*-tolualdehyde (4.77 g, 24 mmol), *m*-tolualdehyde (0.943 mL, 8 mmol), and dry pyrrole (2.2 mL, 32 mmol) in dry chloroform (2.8 L). The reaction mixture was stirred at room temperature for 1.0 h. Triethylamine (2.0 mL, 14 mmol) and then tetrachloro-1,4-benzoquinone (6 g, 25 mmol) were added, and the resulting solution was heated at 60 °C for 45 min. The reaction mixture was evaporated, and the resulting purple solid was triturated with ether and filtered and the filtrate evaporated. The resulting residue was dissolved in a minimum amount of chloroform and was subjected to flash chromatography using silica gel and eluting with a mixture of ethyl acetate/hexanes (0.5:10). Four fractions were obtained: the mono-, the di-, the tri-, and the tetrabromo-*m*-tolylporphyrin. A total of 0.9 g (12%) of the desired product, the tribromo-*m*-tolylporphyrin **3**, was obtained as a purple solid: $^1$H-NMR ($CDCl_3$) δ −2.69 (s, 2 H, NH), 4.68 (s, 6 H, $CH_2Br$), 7.63 (d, 1 H, $J$ = 7.5 Hz, H-4′), 7.67 (t, 1 H, $J$ = 7.5 Hz, H-5′), 7.73 (t, 3 H, $J$ = 7.5 Hz, H-5), 7.80 (d, 3 H, $J$ = 7.5 Hz H-4), 8.08 (d, 3 H, $J$ = 7.5 Hz, H-6′), 8.11 (s, 1 H, H-2′), 8.21 (d, 3 H, $J$ = 7.5 Hz, H-6), 8.93 (6 H, β-pyrrolic H), 8.98 (2 H, β′-pyrrolic H); $^{13}$C-NMR ($CDCl_3$) δ 21.62 ($CH_3$), 33.53 ($CH_2Br$) 119.37 (meso), 120.83, 126.51, 126.97, 127.16, 128.51, 130.03 (β-pyrrolic), 131.85, 134.50, 135.04, 135.48, 136.15, 136.38, 141.85, 142.59; FABMS 908.3 (calcd for $C_{48}H_{36}Br_3N_4$ [M + 1] $m/z$ 908.3); UV/vis ($CHCl_3$) $\lambda_{max}$ ($\epsilon \times 10^{-3}$ $cm^{-1}$ $M^{-1}$) 419 (397), 515 (15.6),

551 (6.1), 591 (4.0), 647 (2.3); emission ($CHCl_3$) $\lambda_{max}$, nm (rel intens) 650.1 (9.85), 713.3 (1.0).

**3-Pyridinesulfonyl chloride** was obtained as previously described:[1c] white powder, mp 138–140 °C (lit.[4a] mp 141–144 °C); IR (Nujol) 1625 (m, C=C), 1590 (m, C=N), 1180–1190, 1100 (s, $SO_2$); $^1$H-NMR (DMSO-$d_6$) $\delta$ 8.07 (t, 1 H, $J$ = 8 Hz, H-5″), 8.67 (d, 1 H, $J$ = 8 Hz, H-6″), 8.88 (s, 1 H, N-H), 9.08 (d, 1 H, $J$ = 6 Hz, H-4″), 9.16 (s, 1 H, H-2″); $^{13}$C-NMR (DMSO-$d_6$) $\delta$ 128.2, 138.7, 142.5, 143.2, 147.0.

**3-Pyridinesulfonamide** was prepared as previously described:[1c] yellow powder, mp 108–110 °C (lit.[4b] mp 110–111 °C); IR (KBr) 3320 (m, NH), 1590 (m, C=C), 1570 (w, C=N), 1180, 1120 (s, $SO_2$); $^1$H-NMR (DMSO-$d_6$) $\delta$ 7.56 (br s, 2 H, NH), 7.62 (dt, 1 H, $J$ = 7.3 Hz), 8.18 (dd, 1 H, $J$ = 8.2 Hz), 8.78 (dd, 1 H, $J$ = 6.1 Hz), 8.97 (d, 1 H, $J$ = 2.5 Hz); $^{13}$C-NMR (acetone-$d_6$) $\delta$ 123.4, 133.4, 146.3, 146.7, 152.0; FABMS 159 (calcd for $C_5H_6N_2O_2S$ [M + 1] $m/z$ 159).

**Reaction of 5,10,15-Tris(α-bromo-*m*-tolyl)-20-*m*-tolylporphyrin, 3, with *m*-Pyridinesulfonamide in the Presence of Excess Cesium Carbonate.** Cesium carbonate (938 mg, 2.88 mmol) was added to a solution containing **3** (474 mg, 0.48 mmol) and *m*-pyridinesulfonamide (114 mg, 0.72 mmol) in dry DMF (480 mL). The reaction mixture was stirred at room temperature overnight and then evaporated to dryness. The purple solid obtained was dissolved in chloroform (50 mL), filtered, and evaporated. The resulting purple residue was subjected to flash chromatography using silica gel and eluting with chloroform. The nonpolar purple bands were collected, and the residue obtained was divided into eight fractions and each fraction was subjected to preparative TLC on a 0.5- × 200- × 200-mm silica plate eluting with chloroform. Two bands were collected and were treated with trifluoroacetic acid (1 mL). The resulting green solution of each of the bands was diluted with chloroform, washed with 5% aqueous ammonium hydroxide solution, water, and brine, dried over anhydrous $Na_2SO_4$, and evaporated to give a purple powder. The polar band gave 35 mg (7%) of **1a** as a purple solid and the nonpolar band gave 17 mg (3.4%) of **1b** as a purple powder. **1a**: $^1$H-NMR ($CDCl_3$) $\delta$ −3.92 (s, 4 H, NH), 2.46, 2.53, 2.56 (s, 6 H, $CH_3$), 4.65, (m, 8 H, $CH_2$(R)), 4.85, (s, 4 H, $CH_2$(R′)), 7.00 (s, 6 H, H-2′), 7.42, 7.44 (s, s, 2 H, H-2‴), 7.47 (broad s, 2 H, H-4‴), 7.53 (broad s, 7 H, H-6″, H-5‴, H-5′(R′)), 7.59 (d, 2 H, $J$ = 8 Hz, H-6‴), 7.65 (t, 4 H, $J$ = 6.5 Hz, H-5′ (R)), 7.79 (broad s, 6 H, H-4′(R′), H-4′(R)), 8.19 (d, 4 H, $J$ = 6 Hz, H-6′(R)), 8.22 (broad s, 7 H, H-5″, β-pyrrolic H), 8.30 (d, 2 H, $J$ = 7.5 Hz, H-6′(R′)), 8.41 (s, 12 H, β-pyrrolic H), 8.77 (broad s, 3 H, H-4″), 9.07, 9.19 (broad s, s, 3 H, H-2″); $^{13}$C NMR ($CDCl_3$) $\delta$ 21.44 ($CH_3$), 49.65 ($CH_2$), 118.18, 120.12 (meso), 123.55 (C6‴), 126.12, 126.65, (C2‴), 127.35 (C5′), 128.30 (C4‴), 128.66 (C4′), 130.23 (β-pyrrolic), 131.28, 131.63 (C5‴), 132.66 (C3′), 133.19 (C6′), 133.74 (C4′), 134.83 (C6‴, C5″, C6′), 135.23 (C-5′), 135.99 (C-3‴), 138.0 (C1‴), 141.23 (C1′), 142.13 (C1′), 148.17, 148.29 (C2″), 153.02, 153.19 (C4″); FABMS 1803.5 (calcd for $C_{111}H_{83}N_{14}O_6S_3$ [M + 1] $m/z$ 1803.5); UV/vis ($CHCl_3$) $\lambda_{max}$ ($\epsilon \times 10^{-3}$ cm$^{-1}$ M$^{-1}$) 406 (sh, 307), 414 (472), 515 (21.3), 550 (8.1), 590 (5.8), 648 (3.2); emission ($CHCl_3$) $\lambda_{max}$, nm (rel intens) 650.1 (8.25), 713.3 (1.0).

**1b**: $^1$H-NMR ($CDCl_3$) $\delta$ −3.32 (s, 4 H, NH), 2.51, 2.72 (broad s, broad s, 6 H, $CH_3$) 3.67 (d, 2 H, $J$ = 15 Hz, $CH_2$b($R_2$), 3.87 (d, 2 H, $J$ = 14.5 Hz, $CH_2$b($R_1$A), 4.19 (d, 2 H, $J$ = 15 Hz, $CH_2$b($R_1$B), 4.82 (d, 2 H, $J$ = 14.5 Hz, $CH_2$a($R_2$), 4.99 (d, 2 H, $J$ = 14.5 Hz, $CH_2$a($R_1$A), 5.12 (d, 2 H, $J$ = 15 Hz, $CH_2$a($R_1$B), 6.27 (s, 2 H, H-2′$R_2$), 6.88 (s, 2 H, H-2′$R_1$A), 7.24 (sh of chloroform, H-2′$R_1$B), 7.44 (broad s, H-6‴), 7.45 (t, $J$ = 7.5 Hz, H-5′$R_1$B), 7.46 (overlapped with H-5′, H-4′$R_2$B), 7.47 (t, $J$ = 7.5 Hz, H-5′$R_1$A), 7.54 (td, $J$ = 7.5, 1 Hz, H-5‴), 7.56 (s, H-2‴), 7.65 (overlapped with H-5′, H-4′$R_2$A), 7.66 (t, $J$ = 7.5 Hz, H-5′$R_2$A), 7.69 (overlapped with H-4′ and H-5′, H-4‴), 7.80 (broad s, H-4′ $R_1$B, H-4′ $R_1$A, H-5′$R_2$B), 7.88 (broad s, H-6‴), 7.99, 8.00 (broad s, β-pyrrolic), 8.09 (d, $J$ = 7.5 Hz, H-6′$R_1$B), 8.15 (broad s, H-6′$R_1$A), 8.34 (broad s, H-6′$R_2$A, β-pyrrolic), 8.56 (broad s, β-pyrrolic, H-6′$R_2$B), 8.67 (broad s, H-4″), 8.79 (broad s, H-5″), 9.02 (sh H-2′$R_2$), 9.04 (broad s, H-2′$R_1$); FABMS 1803.5 (calcd for $C_{111}H_{83}N_{14}O_6S_3$ [M + 1] $m/z$ 1803.5); UV/vis ($CHCl_3$) $\lambda_{max}$ ($\epsilon \times 10^{-3}$ cm$^{-1}$ M$^{-1}$) 408 (sh, 297), 416 (551), 516 (24.3), 552 (8.7), 591 (6.6), 647 (3.4); emission ($CHCl_3$) $\lambda_{max}$, nm (rel intens) 650.1 (8.58), 713.3 (1.0).

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**Supplementary Material Available:** $^1$H-NMR and $^{13}$C-NMR spectra of porphyrins **1a** and **3** and 2D $^1$H–$^1$H (COSY) for **1b** (10 pages). Ordering information is given on any current masthead page.

## A Convenient Method for Converting Saturated Aldehydes to α,β-Unsaturated Aldehydes Elongated by One Carbon Atom. The Pd(II)-Promoted Oxidation of Methyl Enol Ethers

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In the course of our ongoing research directed toward the synthesis of structurally complex indole alkaloids,[1] we found it necessary to evaluate the various currently available methods for transforming an aliphatic aldehyde, i.e., $RCH_2CHO$ (**I**), into an α,β-unsaturated aldehyde, elongated by one carbon atom, i.e., RCH=CHCHO (**II**) (Scheme I). A number of such methods are, in fact, available. For example, the aldehyde **I** can first be converted into a methyl enol ether by reaction with (methoxymethylene)triphenylphosphorane ($CH_3OCH{=}PPh_3$).[2] Acidic hydrolysis of the methyl enol ether would give a saturated aldehyde whose chain is one unit longer than that of the parent aldehyde. The aldehyde thus obtained can then be converted into the corresponding α,β-unsaturated aldehyde by, for example, (i) introducing a suitable leaving group (e.g., halogen, SR, or SeR[3]) at the position α to the carbonyl group and then inducing β-elimination of the elements of HX, (ii) treating the corresponding trimethylsilyl enol ether or allyl enol carbonate with a Pd(II)[4] or Pd(0)[5] species, or (iii) directly dehydrogenating the aldehyde by treatment with Pd(0)/AgOTf.[6] Alternatively, trimethylsilyl cyanide can be added to the aldehyde **I**[7] and the resultant α,β-unsaturated nitrile can be converted to **II**, or the Shapiro reaction[8] can be applied to **I**. However, all these methods for preparing **II** from **I** require three or more steps and the imposition of relatively stringent reaction conditions. If a direct conversion of methyl enol ethers **III**, which can be easily obtained by the Wittig reaction of $CH_3OCH{=}PPh_3$ and aldehydes **I**, into α,β-unsaturated aldehydes **II** can be effected, then an expeditious method for achieving the desired transformation will have been found.

The belief that methyl enol ethers could be transformed into α,β-unsaturated aldehydes was inspired by the work of Saegusa et al.,[4] who found that the silyl enol ethers of saturated ketones could be dehydrosilylated to α,β-un-

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