JOC*Note*

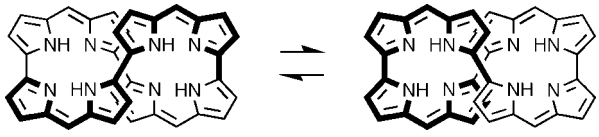
Dynamic Figure Eight Loop Structure of *meso*-Tetraaryl[32]octaphyrins(1.0.1.0.1.0.1.0)

Megumi Mori, Toshifumi Okawa, Noriko Iizuna, Kana Nakayama, Juha M. Lintuluoto,[†] and Jun-ichiro Setsune*

Department of Chemistry, Graduate School of Science, Kobe University, Nada-ku, Kobe 657-8501, Japan

setsunej@kobe-u.ac.jp

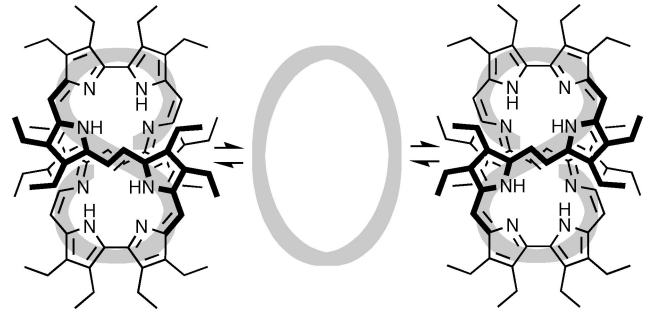
Received January 18, 2009



3,3′-Diethyl substituents of the 2,2′-bipyrrole components in *meso*-tetraaryl[32]octaphyrins(1.0.1.0.1.0.1.0) affect the cavity shape through CH/π interactions and remarkably accelerate *syn*−*anti* conformational change of the 2,2′-bipyrrole components leading to helicity change in the figure eight loop of [32]octaphyrins.

Octaphyrins are composed of eight pyrrole units and some structural variations in the number of π-electrons (30, 32, 34, 36, and 38) and of bridging *meso*-like carbons (0, 2, 4, 6, and 8) are known.[1−5] The π-conjugation systems of octaphyrins in a helical figure eight conformation are of great interest.[2,3] For example, Osuka reported octaphyrin metal complexes with Möbius aromaticity,[6] inspired by a detailed analysis of twisted π-systems of octaphyrins in the design of Möbius molecules by Herges.[7] The unique stereochemical feature of octaphyrins has potential application to chirality sensing and asymmetric catalysis. In fact, we have reported that these octaphyrins can undergo unidirectional helicity induction by reversible complexation with optically active carboxylic acids,[3e] or by irreversible metalation in the presence of optically active ancillary ligand.[3f] Understanding dynamics of the figure eight conformational change is fundamental for further exploring the stereochemical aspect of octaphyrins, and thus the inversion barriers of the figure eight loop in the [34]-octaphyrin(1.1.1.0.1.1.1.0) and [36]octaphyrin(2.1.0.1.2.1.0.1) were estimated by Vogel and co-workers to be at least 85 kJ mol^{-1}.[2b,c] As a matter of fact, enantiomeric separation of the latter was successfully performed.[2c] These octaphyrins are made of two pairs of different dipyrrolic components and the inversion of the helical figure eight loop requires unwinding of the molecular twist followed by rewinding in the opposite way as depicted in Scheme 1.

SCHEME 1. Unwinding−Rewinding Helicity Change in the [36]Octaphyrin(2.1.0.1.2.1.0.1)



In contrast, it was shown that 2,3,6,7,11,12,15,16,20,21,24,25,29,30,33,34-hexadecaethyl[32]octaphyrin(1.0.1.0.1.0.1.0) **1a** having four parts of 3,3′,4,4′-tetraethyl-2,2′-bipyrrole was rapidly interchanging between the figure eight enantiomeric forms and the theoretically estimated inversion barrier was as low as 25 kJ mol^{-1}.[2c] This helicity change of **1a** occurs with keeping diastereotopicity of the CH_2 protons at the pyrrole β-position, which is not consistent with the unwinding−rewinding mechanism. The helicity change is enabled by an alternating stretching−compressing distortion of the rhombic cavity that is enclosed by four panels of the planar dipyrrin unit connected with four hinges in the form of bipyrrole C2−C2′ bonds (Scheme 2). That is, stretching along a shorter diagonal axis of the rhombic cavity accompanied by compressing along a longer diagonal axis leads to a mirror image, whereby a bisdipyrrin unit drawn with a heavy black line in Scheme 2 is interchanging between *anti* and *syn* conformation. Vogel originally described that the two enantiomers are interchanging via "tub" conformation like cyclooctatetraene,[2b] but its detailed dynamic feature has remained to be clarified.

[†] Present address: Department of Synthetic Chemistry and Biochemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan.

(1) (a) Sessler, J. L.; Seidel, D. *Angew. Chem., Int. Ed.* **2003**, *42*, 5134–5175. (b) Latos-Grańyński, L. *Angew. Chem., Int. Ed.* **2004**, *43*, 5124–5128.

(2) (a) Vogel, E.; Bröring, M.; Fink, J.; Rosen, D.; Schmickler, H.; Lex, J.; Chan, K. W. K.; Wu, Y. D.; Plattner, D. A.; Nendel, M.; Houk, K. N. *Angew. Chem., Int. Ed.* **1995**, *34*, 2511–2514. (b) Bröring, M.; Jendrny, J.; Zander, L.; Schmickler, H.; Lex, J.; Wu, Y. D.; Nendel, M.; Chen, J. G.; Plattner, D. A.; Houk, K. N.; Vogel, E. *Angew. Chem., Int. Ed.* **1995**, *34*, 2515–2517. (c) Werner, A.; Michels, M.; Zander, L.; Lex, J.; Vogel, E. *Angew. Chem., Int. Ed.* **1999**, *38*, 3650–3653. (d) Vogel, E.; Michels, M.; Zander, L.; Lex, J.; Tuzun, N. S.; Houk, K. N. *Angew. Chem., Int. Ed.* **2003**, *42*, 2857–2862. (e) Bley-Escrich, J.; Gisselbrecht, J.-P.; Michels, M.; Zander, L.; Vogel, E.; Gross, M. *Eur. J. Inorg. Chem.* **2004**, *49*, 2–499.

(3) (a) Setsune, J.; Maeda, S. *J. Am. Chem. Soc.* **2000**, *122*, 12405–12406. (b) Setsune, J.; Katakami, Y.; Iizuna, N. *J. Am. Chem. Soc.* **1999**, *121*, 8957–8958. (c) Setsune, J.; Mori, M.; Okawa, T.; Maeda, S.; Lintuluoto, J. M. *J. Organomet. Chem.* **2007**, *692*, 166–174. (d) Mori, M.; Setsune, J. *Chem. Lett.* **2007**, *36*, 244–245. (e) Lintuluoto, J. M.; Nakayama, K.; Setsune, J. *Chem. Commun.* **2006**, *69*, 3492–3494. (f) Setsune, J.; Tsukajima, A.; Okazaki, N.; Lintuluoto, J. M.; Lintuluoto, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 771–775.

(4) (a) Seidel, D.; Lynch, V.; Sessler, J. L. *Angew. Chem., Int. Ed.* **2002**, *41*, 1422–1425. (b) Sessler, J. L.; Seidel, D.; Lynch, V. *J. Am. Chem. Soc.* **1999**, *121*, 11257–11258.

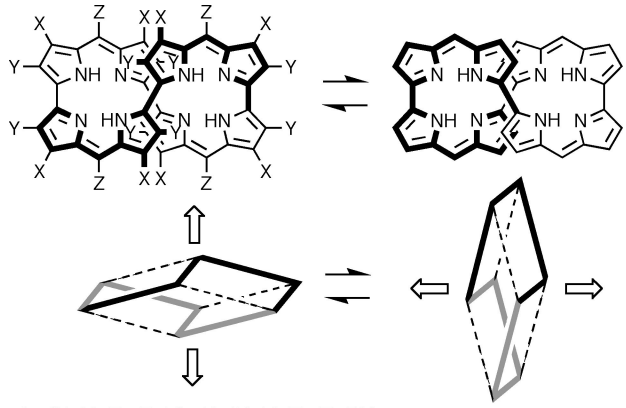
(5) (a) Shimizu, S.; Shin, J.-Y.; Furuta, H.; Ismael, R.; Osuka, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 78–82. (b) Shin, J.-Y.; Furuta, H.; Yoza, K.; Igarashi, S.; Osuka, A. *J. Am. Chem. Soc.* **2001**, *123*, 7190–7191. (c) Geier, G. R., III; Grindrod, S. C. *J. Org. Chem.* **2004**, *69*, 6404–6412.

(6) Tanaka, Y.; Saito, S.; Mori, S.; Aratani, N.; Shinokubo, H.; Shibata, N.; Higuchi, Y.; Yoon, Z. S.; Kim, K. S.; Noh, S. B.; Park, J. K.; Kim, D.; Osuka, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 681–684.

(7) Herges, R. *Chem. Rev.* **2006**, *106*, 4820–4842.

10.1021/jo9001189 CCC: $40.75 © 2009 American Chemical Society
Published on Web 03/27/2009

SCHEME 2. Stretching−Compressing Helicity Change in the [32]Octaphyrins(1.0.1.0.1.0.1.0)



1a (X=Y=Et, Z=H); **1b** (X=Y=Et, Z=Ph); **1c** (X=Me, Y=Et, Z=Ph); **1c'** (X=Me, Y=Et, Z=3,5-$(OMe)_2C_6H_3$); **1d** (X=Et, Y=Me, Z=Ph); **1e** (X=Me, Y=i-Bu, Z=Ph)

We have already shown that *meso*-tetraaryl[32]octaphyrins-(1.0.1.0.1.0.1.0) are obtainable by the Rothemund-type reaction of 2,2′-bipyrrole and arylaldehyde under acidic conditions or by the "2+2" type condensation reaction of 2,2′-bipyrrole and the corresponding bisazafulvene under neutral conditions.[3a−c,8] The latter synthetic method reliably affords *meso*-tetraaryl[32]-octaphyrins(1.0.1.0.1.0.1.0) as a main product. In the present work, four *meso*-tetraphenyl[32]octaphyrins(1.0.1.0.1.0.1.0), **1b**,[3a,b] **1c**, **1d**,[3c] and **1e**,[3c] with different alkyl substituents on the 2,2′-bipyrrole components were used to investigate the dynamics of the figure eight loop inversion. *meso*-Tetra(3,5-dimethoxyphenyl)[32]octaphyrin(1.0.1.0.1.0.1.0) **1c′** that is suited for the VT NMR study because of its much better solubility than **1c** was also prepared from 3,3′-diethyl-4,4′-dimethyl-2,2′-bipyrrole by way of 5,5′-di(3,5-dimethoxybenzoyl)-3,3′-diethyl-4,4′-dimethyl-2,2′-bipyrrole **2c′** and 6,6′-di(3,5-dimethoxyphenyl)-3,3′-diethyl-4,4′-dimethyl-2,2′-bisazafulvene **3c′**.

Variable-temperature ^{1}H NMR in d_8-toluene of **1b** and **1c′** having four parts of 3,3′,4,4′-tetraethyl-2,2′-bipyrrole and 3,3′-diethyl-4,4′-dimethyl-2,2′-bipyrrole, respectively, showed only one set of signals for the 2,2′-bipyrrole units even at −60 °C (Figure 1 and Supporting Information). Therefore, the *syn*−*anti* conformational change of the 2,2′-bipyrrole units is very fast on the NMR time scale for **1b** and **1c′** as well as for **1a**. Since the 3,3′- and 4,4′-diethyl groups appeared as a ABX_3 pattern, stretching−compressing helicity change is taking place.

In contrast, ^{1}H NMR in d_8-toluene of **1d** having four parts of 4,4′-diethyl-3,3′-dimethyl-2,2′-bipyrrole showed two singlets at 2.90 and 1.94 ppm at −40 °C (Figure 2). They are associated with the 3,3′-dimethyl protons of the 2,2′-bipyrrole units in the *syn* and *anti* conformations. These two singlets coalesced at 40 °C and gave a broad singlet at 2.29 ppm at 80 °C. Since signals due to the 4,4′-diethyl groups of **1d** appear as a ABX_3 pattern (1.91, 1.62, 0.72 ppm) at 80 °C, stretching−compressing helicity change is taking place. The activation energy ($\Delta G^{\ddagger}_{313}$) calculated on the basis of the coalescence temperature and the frequency difference between the two exchanging methyl sites is 61.3 kJ mol^{-1}.[9a] This helicity change of **1d** was further studied by the spin saturation transfer experiment (Supporting Information),[9b]

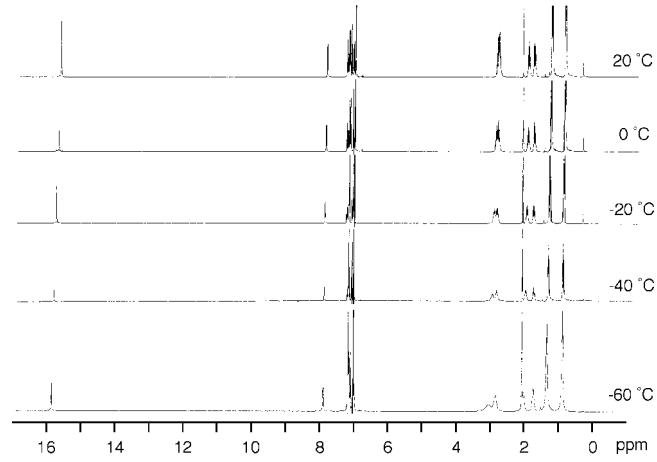


FIGURE 1. Variable-temperature ^{1}H NMR spectra of **1b** in toluene-d_8 in the range −60 to 20 °C.

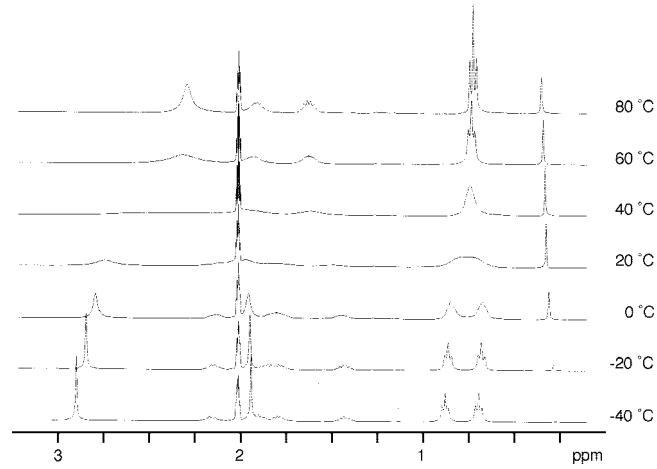


FIGURE 2. Variable-temperature ^{1}H NMR spectra of **1d** in toluene-d_8 in the range −40 to 80 °C.

which gave activation parameters $\Delta H^{\ddagger}$ (65.0 ± 1.3 kJ mol^{-1}) and $\Delta S^{\ddagger}$ (17.5 ± 0.4 J K^{-1} mol^{-1}). The $\Delta G^{\ddagger}_{313}$ value calculated by using these two parameters was 59.5 kJ mol^{-1}, which is in good agreement with the value based on the ^{1}H NMR signal coalescence shown above. It is remarkable that the coalescence temperature of **1b** and **1d** differs by more than 100 °C, which corresponds to the difference of activation energy by at least ca. 20 kJ mol^{-1}.

^{1}H NMR in d_8-toluene at −20 °C of **1e** having four parts of 3,3′-diisobutyl-4,4′-dimethyl-2,2′-bipyrrole also showed two singlets at 1.66 and 1.36 ppm due to the 4,4′-dimethyl protons of the 2,2′-bipyrrole units in the *syn* and *anti* conformations. These two singlets coalesced at 30 °C to lead to a singlet at 1.45 ppm at 60 °C, which is indicative of similar site-exchanging rate of **1e** to that of **1d** (Supporting Information). The activation energy ($\Delta G^{\ddagger}_{303}$) of **1e** calculated on the basis of the coalescence temperature and the frequency difference between the two exchanging methyl sites is 62.2 kJ mol^{-1}. These results indicate that the 3,3′-diethyl groups of the 2,2′-bipyrrole components drive the helicity change of the [32]octaphyrin(1.0.1.0.1.0.1.0) much faster than the less bulky 3,3′-dimethyl groups and the more bulky 3,3′-diisobutyl groups.

X-ray crystallography of **1e** shows that all the isobutyl groups at the 3,3′-positions of the *anti*-2,2′-bipyrrole units at the figure eight crossing point are pushed out of the cavity (Figure 3, right),

(8) Setsune, J.; Tanabe, A.; Watanabe, J.; Maeda, S. *Org. Biomol. Chem.* **2006**, *4*, 2247–2252.

(9) (a) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228–1234. (b) Jarek, R. L.; Flesher, R. J.; Shin, S. K. *J. Chem. Educ.* **1997**, *74*, 978–982.

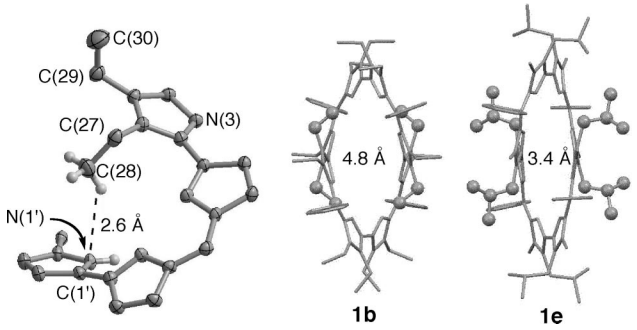


FIGURE 3. Transannular close contact between C(28)-H and N(1′) seen in the partial X-ray structure of **1b** (left); X-ray structures of **1b** (center) and **1e** (right). Ethyl and isobutyl groups at the crossing point are shown by a ball-and-stick model.

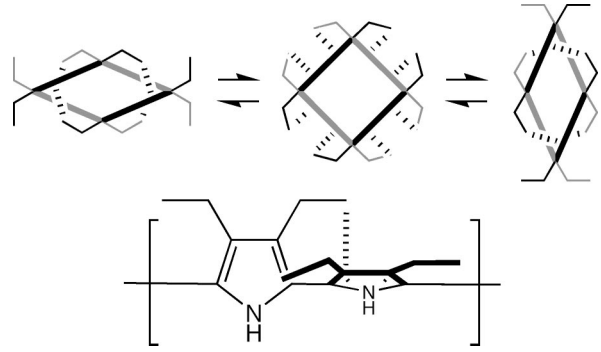
so that the *anti*-2,2′-bipyrrole units come close together in the region (3.4 Å) of van der Waals contact. This rhombic cavity shape of **1e** has a maximum overlap of π-orbitals along the figure eight loop conformation. On the other hand, X-ray crystallography of **1a** and **1b** indicates that all the 3,3′-diethyl groups of the *anti*-2,2′-bipyrrole units at the crossing point of the figure eight loop are directed inside the cavity (Figure 3, center).[2b,3e] Figure 3 (left) shows that the ethyl terminal carbon C(28) attached to the N(3)-pyrrole of **1b** is positioned 3.418 Å from the pyrrole nitrogen N(1′). One of the methyl protons C(28)-H at an ideal *gauche* position is right over the N(1′) atom at a distance of ca. 2.6 Å. This is in the range of the van der Waals contact between N and H atom. There are four such transannular CH/π interactions[10] with the same geometry. The transannular distances 4.6 and 4.8 Å at the figure eight crossing point of **1a** and **1b**, respectively, are longer than that of **1e**. Actually, a torsion angle N−C_α−C_α−N (34.9° on average) in the *syn*-2,2′-bipyrrole units of **1b** is larger than that (21.6°) of **1e** and a torsion angle N−C_α−C_α−N (148.1°) in the *anti*-2,2′-bipyrrole units of **1b** is smaller than that (161.1° on average) of **1e**.

The UV−vis absorption maximum of **1d** at 578 nm is very similar to that of **1e** at 580 nm in CH_2Cl_2, but it is red-shifted with respect to that of **1b** and **1c** at 570 nm. These spectral features suggest that **1d** has a π-conjugation system enclosing a narrower rhombic cavity like that of **1e** and that **1c** has a π-conjugation system enclosing a wider rhombic cavity like that of **1b** as seen in the X-ray crystallography. Similar site-exchanging rates and UV−vis absorption maxima of **1d** and **1e** suggest that the steric crowding of the 3,3′-dialkyl groups does not affect much the shape of the rhombic cavity and the dynamics of the helicity change. The decrease in the π-conjugation of **1b** relative to **1d** and **1e** seems to be compensated by the quadruple CH/π interactions of the ethyl terminal protons at the figure eight crossing point as noted above.

The transition state in the stretching−compressing motion of [32]octaphyrins would take conformation with a square-shaped cavity where π-conjugation through a bipyrrole 2,2′-bond is cut off (Scheme 3). Molecular modeling suggests that 8-fold CH/π interactions between the β-pyrrolic ethyl terminal protons and the adjacent pyrrole π-systems can take place within the orthogonally twisted 2,2′-bipyrrole units to stabilize the square-shaped transition state in the helicity change. This might

(10) (a) Tsuzuki, S.; Honda, K.; Uchimaru, T.; Mikami, M.; Tanabe, K. *J. Am. Chem. Soc.* **2000**, *122*, 11450–11458. (b) Tsuzuki, S.; Honda, K.; Uchimaru, T.; Mikami, M.; Tanabe, K. *J. Am. Chem. Soc.* **2000**, *122*, 3746–3753.

SCHEME 3. A Model for Transition State Conformation with a Square-Shaped Cavity (top) Stabilized by CH/π Interactions of the Ethyl Terminal Protons and the Pyrrole Rings (bottom)



explain the reason why ethyl groups at the 3,3′-position of the 2,2′-bipyrrole units are remarkably promoting helicity change of the [32]octaphyrins.

In summary, the substitution pattern of peripheral alkyl groups of [32]octaphyrin(1.0.1.0.1.0.1.0) has a great influence not only on the conformation but also on the dynamics of the figure eight loop. The present finding on the helicity change of [32]octaphyrins is of valuable in their application to chirality-related functional materials.

Experimental Section

5,5′-Di(3,5-dimethoxybenzoyl)-3,3′-diethyl-4,4′-dimethyl-2,2′-bipyrrole (2c′). $POCl_3$ (0.78 mL, 8.4 mmol) was added by syringe to *N*,*N*-dimethyl-3,5-dimethoxybenzamide (1.67 g, 8.0 mmol) under argon and the mixture was stirred for 2 h at room temperature to afford yellow solid. To this reaction mixture was added 3,3′-diethyl-4,4′-dimethyl-2,2′-bipyrrole (346 mg, 1.60 mmol) dissolved in 1,2-dichloroethane (7.9 mL) through syringe. The resulting solution was stirred under argon overnight, and then heated at 70−80 °C with stirring for 6 h. After K_2CO_3 aqueous solution (4.6 g/8 mL) was added carefully, the mixture was refluxed for 3 h and then partitioned between CH_2Cl_2 and water. The organic layer was dried over anhydrous K_2CO_3 and then evaporated under vacuum. The residue was chromatographed on silica gel with CH_2Cl_2−acetone (5:1). The red fraction was collected and recrystallized from CH_2Cl_2−hexane to give pale violet powders (680 mg, 1.25 mmol). Yield 78%. ^{1}H NMR (400 MHz, δ value, in $CDCl_3$) 8.80 (br, 2H), 6.82 (s, 4H), 6.62 (s, 2H), 3.84 (s, 12H), 2.54 (q, 4H), 2.15 (s, 6H), 1.11 (t, 6H). ESI-MS (found/calcd for $C_{32}H_{36}N_2O_6 + H^+$) 545.17/545.27. Anal. Calcd for $C_{32}H_{36}N_2O_6$: C, 70.57; H, 6.66; N, 5.14. Found: C, 70.27; H, 6.79; N, 5.22.

6,6′-Di(3,5-dimethoxyphenyl)-3,3′-diethyl-4,4′-dimethyl-2,2′-bisazafulvene (3c′). $NaBH_4$ (890 mg, 23.6 mmol) was added in small portions over 30 min to a stirred solution of 5,5′-di(3,5-dimethoxybenzoyl)-3,3′-diethyl-4,4′-dimethyl-2,2′-bipyrrole (256 mg, 0.47 mmol) in a mixture of MeOH (10 mL) and THF (15 mL) under argon. The resulting reaction mixture was stirred at room temperature for 3 h and then partitioned between CH_2Cl_2 and water. The organic layer was dried over anhydrous K_2CO_3 and then evaporated under vacuum. A mixture of the vacuum-dried crude diol, di-*tert*-butyl dicarbonate (307 mg, 1.41 mmol), and 4-dimethylaminopyridine (2.9 mg, 0.024 mmol) in dry THF (24 mL) was stirred at room temperature for 2 h under argon. The reaction mixture was evaporated under vacuum and the residue was washed with MeOH to give the product (193 mg, 0.38 mmol). Yield 80%. ^{1}H NMR (400 MHz, δ value, in $CDCl_3$) 7.48 (s, 4H), 6.89 (s, 2H), 6.52 (s, 2H), 3.86 (s, 12H), 3.04 (q, 4H), 2.20 (s, 6H), 1.15 (t, 6H). ESI-MS (found/calcd for $C_{32}H_{36}N_2O_4 + H^+$) 513.25/513.28. Anal.

Calcd for $C_{32}H_{36}N_2O_4$: C, 74.97; H, 7.08; N, 5.46. Found: C, 74.98; H, 6.99; N, 5.00.

3,6,12,15,21,24,30,33-Octaethyl-2,7,11,16,20,25,29,34-octamethyl-9,18,27,36-tetra(3,5-dimethoxyphenyl)[32]octaphyrin-(1.0.1.0.1.0.1.0) (1c′). A mixture of 3,3′-diethyl-4,4′-dimethyl-2,2′-bipyrrole (70 mg, 0.325 mmol) and 6,6′-di(3,5-dimethoxyphenyl)-3,3′-diethyl-4,4′-dimethyl-2,2′-bisazafulvene (166 mg, 0.325 mmol) in dry CH_2Cl_2 (8 mL) was stirred at room temperature under argon for 16 h. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (221 mg, 0.975 mmol) was added to the reaction mixture and the resulting blue violet solution was stirred at room temperature for 2 h. After passing through Celite, the CH_2Cl_2 solution was washed with 1% $HClO_4$ aqueous solution and then with 10% NaOH aqueous solution. The organic layer was separated, dried over anhydrous Na_2SO_4, and chromatographed on silica gel with CH_2Cl_2−acetone (10:1). The violet fraction was recrystallized from CH_2Cl_2−MeOH to give **1c′** (35 mg, 0.024 mmol). Yield 15%. ^{1}H NMR (400 MHz, δ value, in $CDCl_3$) 16.02 (s, 4H), 7.34 (s, 8H), 7.22 (s, 4H), 3.76, 3.46 (s × 2, 12H × 2), 3.23, 3.05 (q × 2, 8H × 2), 1.76 (s, 24H), 1.40 (t, 24H). UV−vis (λ_{max} (log ϵ) in CH_2Cl_2) 372.5 (4.51), 572 (4.99) nm. ESI-MS (found/calcd for $C_{92}H_{104}N_8O_8 + H^+$) 1448.80/1448.65. Anal. Calcd for $C_{92}H_{104}N_8O_8$: C, 76.21; H, 7.23; N, 7.73. Found: C, 75.94; H, 7.34; N, 7.67.

3,6,12,15,21,24,30,33-Octaethyl-2,7,11,16,20,25,29,34-octamethyl-9,18,27,36-tetraphenyl[32]octaphyrin(1.0.1.0.1.0.1.0) (1c). Yield 12%. ^{1}H NMR (400 MHz, δ value, in $CDCl_3$) 15.05 (s, 4H), 7.53−7.42 (m, 20H), 2.73, 2.58 (br × 2, 8H × 2), 1.33 (br, 24H), 0.98 (t, 24H). UV−vis (λ_{max} (log ϵ) in CH_2Cl_2) 373 (4.64), 570.5 (5.09) nm. ESI-MS (found/calcd for $C_{84}H_{88}N_8 + H^+$) 1208.71/1208.66. Anal. Calcd for $C_{84}H_{88}N_8 \cdot (CH_3OH)$: C, 80.22; H, 7.46; N, 9.02. Found: C, 80.00; H, 7.47; N, 8.86.

X-ray Crystallography of (1e) $C_{100}H_{120}N_8$. An X-ray diffractometer equipped with a CCD detector was used for data collection. An empirical absorption correction was applied with use of the sadabs program. The structure was solved and refined by full-matrix least-squares calculations on F^2, using the shelxtl 97 program package.[11] $M = 1434.04$, $T = 193(2)$ K, monoclinic, space group $P2(1)/c$, $a = 25.9786(18)$ Å, $b = 16.6372(12)$ Å, $c = 20.7138(14)$ Å, $\beta = 105.2820(10)°$, $V = 8636.2(10)$ Å^3, $Z = 4$, $\rho_{calc} = 1.103$ g cm^{-3}, μ(Mo Kα) = 0.064 mm^{-1}, reflections collected 44038, unique reflections 15589 ($R_{int} = 0.0450$), GOF = 1.049, final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0582$, $wR_2 = 0.1339$, R indices (all data) $R_1 = 0.1230$, $wR_2 = 0.1640$. CCDC reference number 721780.

Acknowledgment. This work was supported by Grant-in-Aid for Scientific Research (No.18550058) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. The author is also grateful to the CREST program (the Japan Science and Technology Agent) and the VBL project (Kobe University).

Supporting Information Available: Outline of the synthetic procedure for **1c** and **1c′** with characterization data for 5,5′-dibenzoyl-3,3′-diethyl-4,4′-dimethyl-2,2′-bipyrrole (**2c**) and 6,6′-diphenyl-3,3′-diethyl-4,4′-dimethyl-2,2′-bisazafulvene (**3c**) as the synthetic precursors of **1c**, details of spin saturation transfer experiment of **1d** including ^{1}H NMR spectra at 243 K in toluene-d_8 with and without irradiation at one of the two exchanging Me signals, and a plot of ln(k/T) as a function of T^{-1}, variable-temperature ^{1}H NMR spectra of **1c′** and **1e** in toluene-d_8 between −60 to 80 °C, and an Ortep drawing of **1e**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO9001189

(11) Sheldrick, G. M. *SHELXTL 5.10 for Windows NT*, Structure Determination Software Programs; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997.