DOI: 10.1002/chem.200601644

Synthesis of Porphyrin Dimers Fused with a Benzene Unit

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Abstract: Bicyclo[2.2.2]octadiene-connected pyrrolo-porphyrins have been prepared by an inverse-type [3+1] porphyrin synthesis of a bicyclo[2.2.2]octadiene-fused dipyrrole with a tripyrrane dicarbaldehyde. Another [3+1] porphyrin synthesis of pyrrole-connected porphyrins with the same or other tripyrrane dicarbaldehydes gave bicyclo[2.2.2]octadiene-bridged diporphyrins, the central metals and/or peripheral substituents of which were different. Thermal decomposition of the bicyclo[2.2.2]octadiene skeleton to a benzene moiety gave π-system-fused porphyrin dimers in a highly pure form.

Keywords: conjugation · dimerization · porphyrinoids · retro-Diels–Alder reaction · stacking interactions

Introduction

Recently, compounds with a highly conjugated π system have attracted much attention as promising organic materials for electronic devices such as organic thin-film transistors.[1] From a synthetic point of view, the assembly of stable, smaller π-system units in the final step is advantageous for the construction of a large π system as compared with sequential expansion of an already quite large π system. This is due to the intrinsic instability towards oxygen and the low solubility in common solvents that result from the highly planar nature of compounds of this type with a large π system. A porphyrin π system is sufficiently large and stable to be used as such a basic unit. Therefore, successful preparative methods for π-system-fused porphyrin dimers have been reported by several groups. These methods may be categorized into a number of classes according to the way in which the fused porphyrin π system is ultimately constructed; that is, by the construction of connecting aromatic moieties by dehydrative condensation,[2] by porphyrin synthesis[3] using pyrrole-fused porphyrins,[3a,b] by dehydrogenative aromatization[4] of a cyclohexadiene moiety between the porphyrin rings, or by oxidative π-system fusion[5] of porphyrins. Difficulties are often encountered in the purification and/or separation of the desired porphyrin dimers from chemical materials such as side products derived from the reagents, residual reagents, and, in some cases, solvents, due to high propensity for stacking of the target molecules. Bulky groups or long alkyl chains have been appended in order to increase solubility in organic solvents so as to facilitate purification by column chromatography or recrystallization. However, the introduction of such groups may have an adverse effect on the electronic properties of the systems in the context of molecular devices by diminishing the intermolecular π-system interaction. We have developed a new synthesis of highly pure π-expanded porphyrins and porphyrinoids based on the final conversion of precursors by a retro-Diels–Alder reaction,[6] and have applied this protocol to the preparation of porphyrin dimers fused with a benzene[7] or anthraquinone[8] unit. In this paper, we discuss another example of the successful use of this method, namely, for the preparation of π-system-fused porphyrin dimers with different central metals and/or peripheral substituents, as well as the structures of these products.

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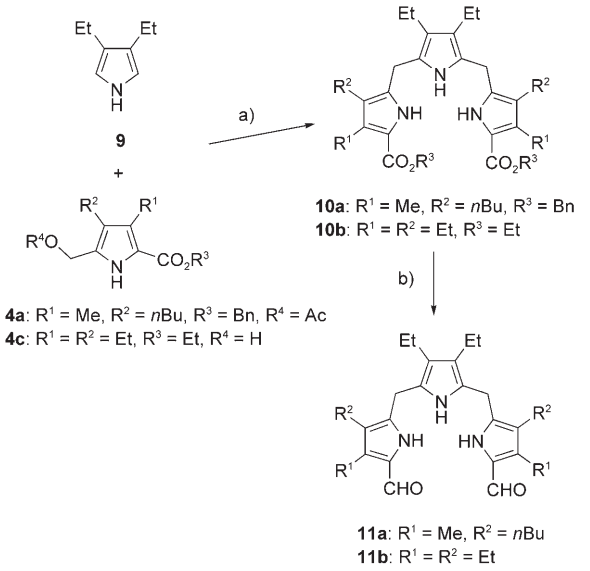
Results and Discussion

Preparation of bicyclo[2.2.2]octadiene-fused porphyrin dimers: Our key precursors are dipyrroles **2** and **3** fused

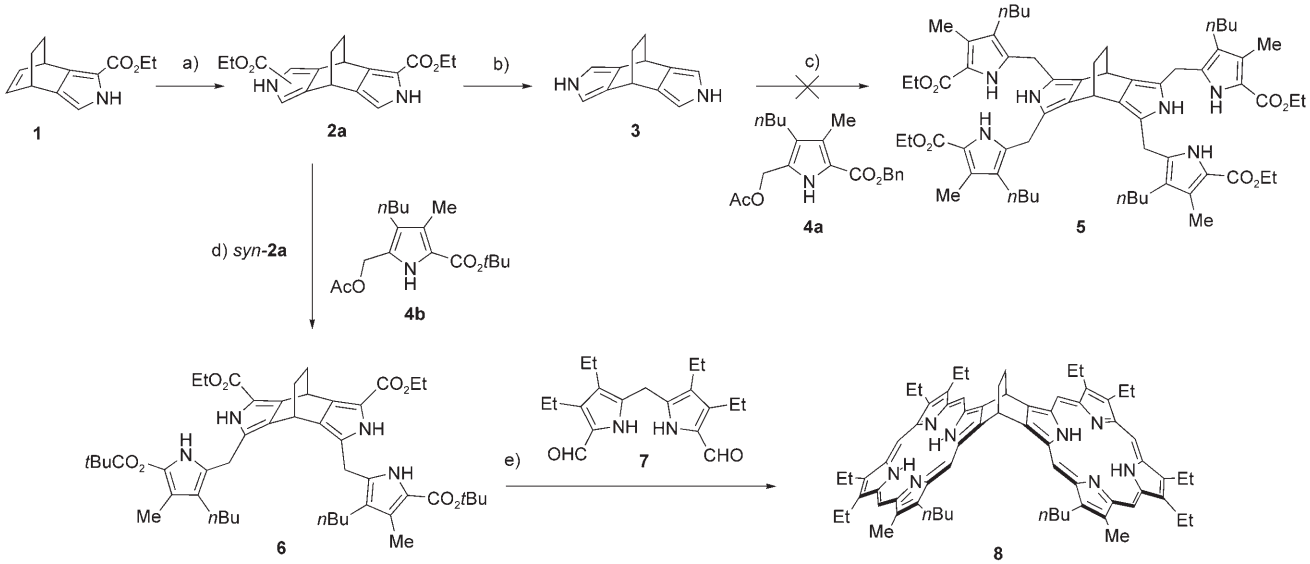
with a bicyclo[2.2.2]octadiene skeleton (Scheme 1). Dipyrrole **2a** was prepared from the bicyclo[2.2.2]octadiene-fused pyrrolecarboxylate ethyl ester **1** by standard construction of another pyrrole ring at the double bond.[9] Removal of the ethyl ester groups from **2a** was achieved by treatment with potassium hydroxide in ethylene glycol at 170 °C to give **3** in 83 % yield. We first attempted to prepare the target porphyrin dimer by a [3+1] porphyrin synthesis involving the bistripyrrane **5**.[10,11] Thus, dipyrrole **3** was treated with 5-(acetoxymethyl)-2-pyrrolecarboxylate benzyl ester **4a** under acidic conditions (*p*-toluenesulfonic acid (*p*-TSA), acetic acid, room temperature). However, none of the desired bistripyrrane was obtained. Next, a route based on [2+2] porphyrin synthesis[11] was examined. Acid treatment of a mixture of *syn*-**2a** and 5-(acetoxymethyl)-2-pyrrolecarboxylate *tert*-butyl ester **4b** gave bis-dipyrromethane **6** in moderate yield. Bis-dipyrromethane **6** was condensed with all-ethyl-substituted dipyrromethane dicarbaldehyde **7** and then the mixture was oxidized with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Although the presence of the target diporphyrin **8** in the reaction mixture was detected by using UV spectroscopy and TOF-MS analyses, we were unable to isolate it.

In order to carry out an inverse-type [3+1] porphyrin synthesis,[8] tripyrrane carbaldehydes[12] such as **11** were required (Scheme 2). 3,4-Diethylpyrrole (**9**) was reacted with 5-(acetoxymethyl)pyrrolecarboxylate esters **4a** and **4c** in the presence of an acid catalyst to give tripyrrane diesters **10a** and **10b** in respective yields of 72 and 29 %.[13] Deprotection of esters **10a** and **10b** followed by formylation with methyl orthoformate in trifluoroacetic acid (TFA) gave the target tripyrrane dicarbaldehydes **11a** and **11b** in yields of 81 and 51 %, respectively.

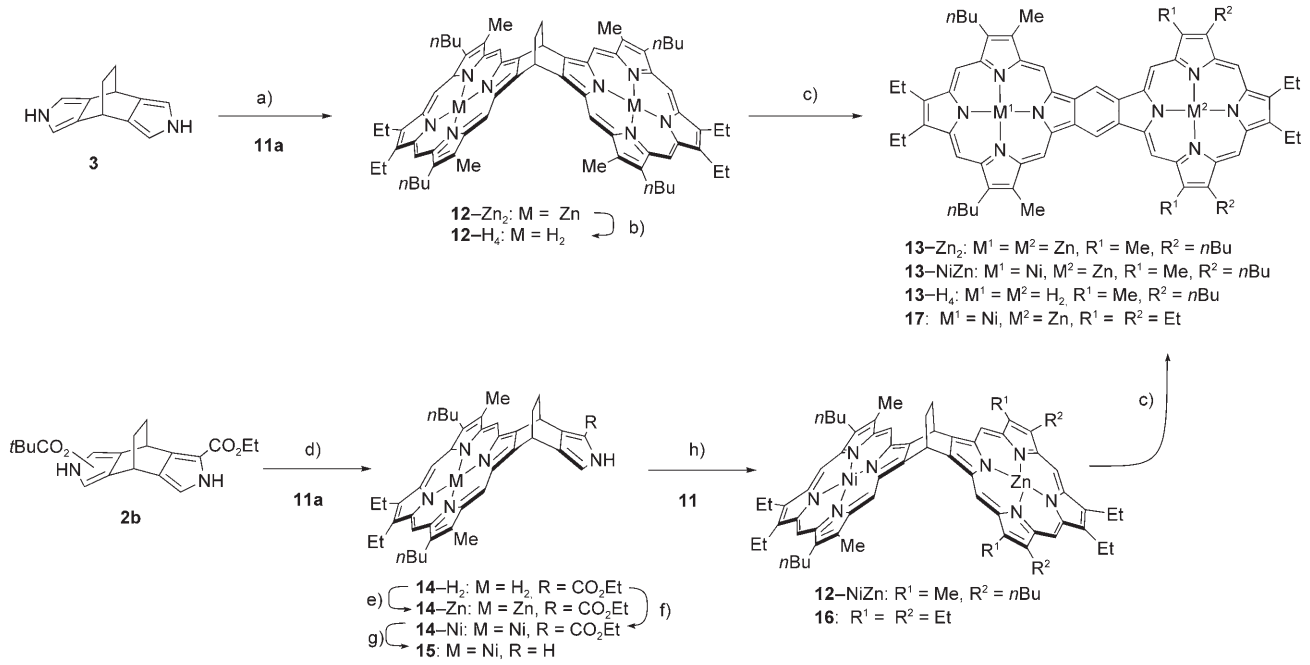


Scheme 2. Preparation of tripyrrane dicarbaldehydes: a) **4a**, AcOH, EtOH; 72 %; or **4c**, *p*-TSA, EtOH; 29 %; b) **10a**, H_2, Pd/C, Et_3N, THF; TFA, $CH(OMe)_3$; 81 %; or **10b**, LiOH, aq. EtOH/THF, 80 °C; TFA, $CH(OMe)_3$; 51 %.

The synthesis of a symmetric diporphyrin was examined using **3** (Scheme 3). Inverse-type [3+1] porphyrin synthesis of **3** with tripyrrane dicarbaldehyde **11a** afforded the bicyclo[2.2.2]octadiene-fused porphyrin dimer **12**-H_4, which was purified as **12**–Zn_2 (21 %) after metalation with zinc acetate.[7] The pure free-base diporphyrin **12**-H_4 was obtained in 98 % yield by demetalation of **12**–Zn_2 with TFA. Next, we planned to prepare porphyrin dimers incorporating different metal atoms and bearing different peripheral substituents. For this purpose, a dipyrrole with differently substituted pyrrole rings was required, for which we chose the *tert*-butyl and ethyl diester of dipyrroledicarboxylate, **2b** (Scheme 3). Applying the standard protocol[9] for the con-



Scheme 1. Early attempts to prepare porphyrin dimers fused with bicyclo[2.2.2]octadiene: a) PhSCl, CH_2Cl_2, −78 °C; 98 %; *m*CPBA, $CHCl_3$, 0 °C; 99 %; *t*BuOK, THF, RT; 99 %; $CNCH_2CO_2Et$, *t*BuOK, THF, −20 °C to RT; 73 %. b) KOH, $(CH_2OH)_2$, 170 °C; 83 %. c) **4a**, *p*-TSA, AcOH. d) *syn*-**2a**, **4b**, *p*-TSA, AcOH; 41 %. e) KOH, $(CH_2OH)_2$, 170 °C; **7**, TFA, CH_2Cl_2; Et_3N; DDQ, CH_2Cl_2; trace.



Scheme 3. Preparation of porphyrin dimers fused with a bicyclo[2.2.2]octadiene unit: a) **11a**, TFA, CH_2Cl_2; Et_3N, CH_2Cl_2; DDQ, CH_2Cl_2; $Zn(OAc)_2{\cdot}2H_2O$, $CHCl_3$; **12**–Zn_2: 21%. b) TFA, $CHCl_3$, RT; 98%. c) heat, quantitative. d) **11a**, TFA, CH_2Cl_2; Et_3N, CH_2Cl_2; DDQ, CH_2Cl_2; 27%. e) $Zn(OAc)_2{\cdot}2H_2O$, $CHCl_3$; 98%. f) $Ni(OAc)_2{\cdot}4H_2O$, $CHCl_3$; 85%. g) KOH, $(CH_2OH)_2$, 180°C; 82%. h) **11a** or **11b**, TFA, CH_2Cl_2; Et_3N, CH_2Cl_2; DDQ, CH_2Cl_2; $Zn(OAc)_2{\cdot}2H_2O$, $CHCl_3$; 12% for **12**–NiZn, 35% for **16**.

struction of a pyrrole ester moiety at a double bond to bicyclo[2.2.2]octadiene-fused pyrrole **1** using *tert*-butyl isocyanoacetate, the target diester **2b** was obtained in 78% yield. When the inverse [3+1] porphyrin synthesis with tripyrrane dicarbaldehyde **11a** was directly applied to the diester **2b**, a porphyrin ring was selectively constructed at the pyrrole ring bearing the *tert*-butyl ester moiety, which was initially removed by the acid treatment. The free-base porphyrin **14**-H_2 was obtained in 27% yield and metalations with zinc acetate and nickel(II) acetate gave the zinc– and nickel–porphyrins **14**–Zn and **14**–Ni in respective yields of 98 and 85%. When we used **14**–Zn as the starting material for another porphyrin-ring construction, partial demetalation occurred during both the ester group removal and the following porphyrin synthesis. Therefore, we employed nickel–porphyrin **14**–Ni to prepare the dimers. Removal of the ester group from **14**–Ni was carried out under basic conditions to give the α-unsubstituted pyrrole-fused porphyrin **15** in 82% yield. Another inverse [3+1] porphyrin synthesis of **15** with tripyrrane dicarbaldehyde **11a**, followed by metalation with zinc acetate, gave the nickel and zinc bis-porphyrin **12**–NiZn in 12% yield. When all-ethyl tripyrrane dicarbaldehyde **11b** was used instead of **11a**, nonsymmetric bis-porphyrin **16** was obtained in 35% yield.

Retro-Diels–Alder π-system fusion: Differential scanning calorimetric analyses of the symmetrical dimers **12**–Zn_2 and **12**–H_4 showed sharp exothermic decomposition peaks at 160 and 170°C (peak widths: 155–175 and 163–178°C at 20°C min^{-1}), respectively. Thermogravimetric (TG) experiments (10°C min^{-1}) were also indicative of quantitative loss of an ethylene unit during this period. Similar results were obtained from TG experiments on the other dimers **12**–NiZn and **16**: sharp weight loss started at 135°C (**12**–NiZn) and 120°C (**16**), the half points of the TG curves were around 165°C (**12**–NiZn) and 156°C (**16**), and in both cases the loss stopped at 175°C. The total weight losses were 2.38% for **12**–NiZn and 2.47% for **16**. These values compare very well with the theoretical values (2.37% for **12**–NiZn and 2.43% for **16**). The somewhat slower decomposition and the slightly greater weight loss observed in the case of the decomposition of precursor **16** were probably due to the inclusion of a small amount of solvent. Preparative conversions of the precursors **12** and **16** were performed at 200°C under reduced pressure (ca. 0.2 mmHg) for 1 h, whereby the π-conjugated dimers **13** and **17** were obtained in quantitative yields.

Spectroscopic analyses of the bicyclo[2.2.2]octadiene-bridged porphyrin oligomers: In the ^{1}H NMR spectrum of the symmetric bicyclo[2.2.2]octadiene-bridged dimer **12**–Zn_2 ($CDCl_3$), the signals of two *meso*-protons were observed at $\delta = 10.83$ (inner) and 10.01 ppm (outer), while that of the bridgehead proton was seen at $\delta = 7.88$ ppm due to a summation of the large anisotropic effects of the porphyrin ring currents. In the spectrum of the bicyclo[2.2.2]octadiene-bridged dimer **12**–NiZn, four *meso*-proton signals were observed at $\delta = 10.56$ (inner *meso*-proton of the Ni porphyrin unit), 10.55 (inner *meso*-proton of the Zn porphyrin unit), 9.72 (outer *meso*-proton of the Zn porphyrin unit), and

9.31 ppm (outer *meso*-proton of the Ni porphyrin unit), along with a bridgehead proton signal at $\delta = 7.70$ ppm. The corresponding signals for the nonsymmetric bis-porphyrin **16** were seen at $\delta = 10.72$, 10.49, 9.98, 9.75, and 7.69 ppm, respectively.

The absorption and fluorescence spectra of the dimers are shown in Figure 1. Soret and Q bands of the zinc- and nickel-porphyrin monomers **14**–Zn and **14**–Ni were observed at similar positions [λ ($\log\varepsilon$) = 403 (5.49), 532 (4.19), and 570 nm (4.24) for **14**–Zn (Figure 1e, orange solid line); λ ($\log\varepsilon$) = 394 (5.28), 516 (4.04), and 554 nm (4.37) for **14**–Ni (Figure 1g, blue solid line)] to those of the corresponding octaalkyl-substituted metalloporphyrins. The bicyclo[2.2.2]octadiene-bridged dimer **12**–NiZn exhibits two Soret bands at λ ($\log\varepsilon$) = 394 (5.42) and 410 nm (5.49), and three Q bands at λ ($\log\varepsilon$) = 535 (4.40), 555 (4.53), and 572 nm (4.50) (Figure 1g, turquoise line). Almost the same spectrum was recorded for **16** (Figure 1f, green solid line). The shorter-wavelength Soret-band absorption appeared at almost the same position as in the case of the parent nickel–porphyrin **14**–Ni, with a slightly higher intensity, while the longer-wavelength Soret band absorbed at a lower energy compared with that of the zinc–porphyrin **14**–Zn, with almost the same intensity. Even in the case of the symmetric zinc–porphyrin dimer **12**–Zn_2, two separate Soret bands were observed at 399 and 414 nm with similar intensities ($\log\varepsilon = 5.65$; Figure 1a, navy-blue solid line). This is due to exciton coupling between the porphyrin rings by homo-conjugation through the bicyclo[2.2.2]octadiene moiety.[14] In the case of the symmetric free-base dimer **12**–H_4 in $CHCl_3$, we observed the characteristic four Q bands and very broad Soret bands due to stacking (Figure 1b, magenta solid line). When trifluoroacetic acid was added, the absorption bands of **12**–H_4 became sharp, and two sharp Soret bands were observed at 400 and 419 nm (Figure 1g, brown solid line). These were wider than that (ca. 15 nm) reported for a protonated dimer singly connected by a methylene bridge between the β-positions.[14] This is suggestive of a stronger interaction between the orientationally constrained porphyrin chromophores of protonated **12**–H_4 through the rigid bicyclo[2.2.2]octadiene bridge. Figure 1h shows the fluorescence emission spectra of the dimers: **12**–H_4 in $CHCl_3$ (magenta line), **12**–Zn_2 in $CHCl_3$ (navy-blue line), **13**–H_4 in 1% TFA/$CHCl_3$ (dark green line), **13**–Zn_2 in 1% pyridine/$CHCl_3$ (black line), **14**–Zn in $CHCl_3$ (orange line), and **16** in $CHCl_3$ (green line). Their excitation spectra are shown in Figures 1a–f as dotted lines. The

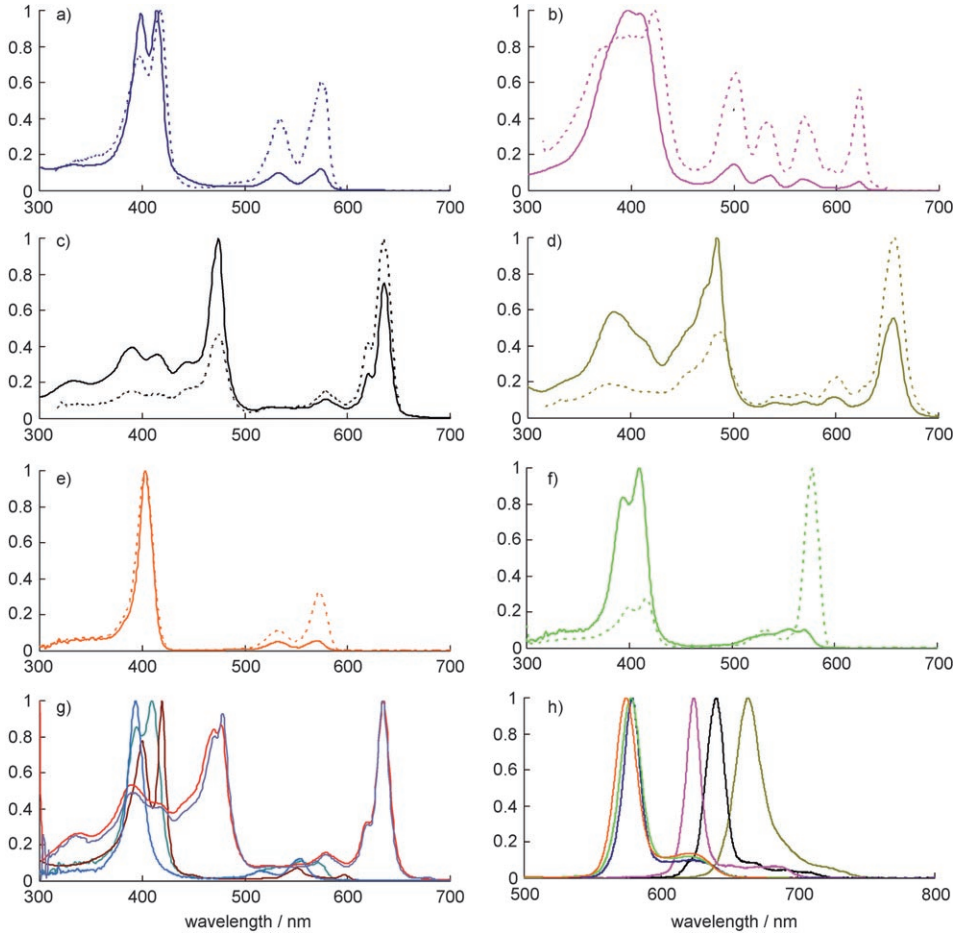


Figure 1. UV/Vis and fluorescence spectra of the porphyrin dimers fused with bicyclo[2.2.2]octadiene and benzene units. a) Absorption spectrum of **12**–Zn_2 in $CHCl_3$ (navy-blue solid line) and excitation spectrum of **12**–Zn_2 in $CHCl_3$ for the 579 nm peak (navy-blue dotted line); b) absorption spectrum of **12**-H_4 in $CHCl_3$ (magenta solid line) and excitation spectrum of **12**-H_4 in $CHCl_3$ for the 624 nm peak (magenta dotted line); c) absorption spectrum of **13**–Zn_2 in 1% pyridine/$CHCl_3$ (black solid line) and excitation spectrum of **13**–Zn_2 in 1% pyridine/$CHCl_3$ for the 640 nm peak (black dotted line); d) absorption spectrum of **13**-H_4 in 1% TFA/$CHCl_3$ (dark green solid line) and excitation spectrum of **13**-H_4 in 1% TFA/$CHCl_3$ for the 663 nm peak (dark green dotted line); e) absorption spectrum of **14**–Zn in $CHCl_3$ (orange solid line) and excitation spectrum of **14**–Zn in $CHCl_3$ for the 575 nm peak (orange dotted line); f) absorption spectrum of **16** in $CHCl_3$ (green solid line) and excitation spectrum of **16** in $CHCl_3$ for the 578 nm peak (dotted green line); g) absorption spectra of **14**–Ni (blue line), **12**-H_4 in 1% TFA/$CHCl_3$ (brown line), **12**–NiZn in $CHCl_3$ (turquoise line), **13**–NiZn (grey line), and **17** in pyridine (red line); h) emission spectra of **12**-H_4 in $CHCl_3$ irradiated at 397 nm (magenta line), **12**–Zn_2 in $CHCl_3$ irradiated at 415 nm (navy-blue line), **13**-H_4 in 1% TFA/$CHCl_3$ irradiated at 658 nm (dark green line), **13**–Zn_2 in 1% pyridine/$CHCl_3$ irradiated at 636 nm (black line), **14**–Zn in $CHCl_3$ irradiated at 403 nm (orange line), and **16** in $CHCl_3$ irradiated at 410 nm (green line).

emission spectrum of the free-base dimer **12**–H_4 shows a sharp fluorescence peak at 624 nm along with a broad band at 682 nm; the Stokes shift is 2 nm (Figure 1h, magenta line). In the emission spectrum of the symmetric zinc dimer **12**–Zn_2, a strong fluorescence peak is observed at 579 nm, along with a weak peak at 624 nm (Figure 1h, navy-blue line). This fluorescence spectrum is very similar to that of **14**–Zn (575 and 621 nm, Figure 1h, orange line). Nickel–porphyrins are well known to show no fluorescence.[15] In the case of the different-metal dimer **16**, we expected that it might be possible to observe fluorescence from the zinc–porphyrin moiety. When we examined dimer **16** in chloroform, a fluorescence peak was observed at 578 nm (Figure 1h, green line). The peak maxima in the excitation spectrum for the 578 nm peak of **16** (Figure 1f, green dotted line) were very similar to those seen in the excitation spectrum of **12**–Zn_2 (Figure 1a, navy-blue dotted line). They were, however, different from those seen in the absorption spectrum of **16** (Figure 1f, solid green line) and in the excitation spectrum of **14**–Zn (Figure 1e, orange dotted line). Although the photomultiplier response was uncorrected in all of the emission spectra, the intensity ratios of the peak maxima for **16** and **12**–Zn_2 were quite different. Therefore, we conclude that this fluorescence from the sample of **16** originated from the zinc–porphyrin moiety.

Spectroscopic analyses of the benzene-fused porphyrin dimers: NMR analyses of the fully conjugated dimers **13** and **17** were carried out. ^{1}H NMR spectra of the symmetric benzene-fused dimers **13**–Zn_2 and **13**–H_4 were successfully recorded in deuterated pyridine and deuterio-chloroform containing 1% trifluoroacetic acid, respectively. The signals of the *meso*-protons of **13**–Zn_2 and **13**–H_2 were observed at lower fields [$\delta = 10.99$ (inner) and 10.15 ppm (outer) for **13**–Zn_2; $\delta = 11.45$ (inner) and 10.64 ppm (outer) for **13**–H_4] compared with those of the precursor dimers **12**–Zn_2 and **12**–H_4 owing to an increase in porphyrin ring current as a result of conjugation. The signals of the protons of the fusing benzene unit appeared at the lowest fields ($\delta =$ 11.48 ppm for **13**–Zn_2, 11.81 ppm for **13**–H_4), while a very broad absorption due to the pyrrolic protons was observed at $\delta = -2.25$ ppm for **13**–H_4. We encountered a difficulty in obtaining NMR data for the nickel and zinc–porphyrin dimers **13**–NiZn and **17** owing to their low solubility in deuterated solvents. Satisfactory ^{1}H NMR spectra could only be obtained for samples in [D_5]pyridine, although their interpretation was rather difficult. In these spectra, only three singlet signals were observed in the low-field region besides the solvent pyridine signals at room temperature, although five singlet signals were expected. No other corresponding signal was found even over 16 ppm (up to 45 ppm). In order to assign these ^{1}H NMR spectra, we measured the spectrum of **13**–NiZn at various temperatures, as illustrated in Figure 2. Although the required signals were sometimes overlapped by a broad water signal, very large residual solvent peaks, and their satellite signals due to coupling with ^{13}C, the protons of the peripheral alkyl groups, the *meso*-protons of the zinc–porphyrin, and those of the benzene unit could be successfully assigned as indicated in Figure 2 with the aid of a COSY experiment at 60 °C. Indeed, very interesting behavior was observed: only the signals due to the protons of the benzene and alkyl groups on the nickel–porphyrin unit were found at very low fields as a result of the large anisotropic effect of the intermolecularly stacked porphyrin rings, and these were shifted upfield as the temperature was increased. On the other hand, the signals of the protons of the zinc–porphyrin unit appeared at similar positions irrespective of the measuring temperature. This phenomenon clearly suggests that only the nickel–porphyrin units of the mixed-metal dimer **13**–NiZn become stacked in deuterated pyridine. Axial coordination of the solvent to the zinc–porphyrin unit apparently prevents stacking of this part of the molecule. In the high-temperature spectra of **13**–NiZn and **17**, broad singlet signals due to two protons appeared at around $\delta = 6.8$ ppm at 80 °C and 5.8 ppm at 60 °C (marked with asterisks in Figure 2), while the corresponding signals were observed at 3.6 ppm at room temperature. We ascribe these signals, which appear at remarkably high fields owing to the anisotropic effect, to one set of *meso*-protons

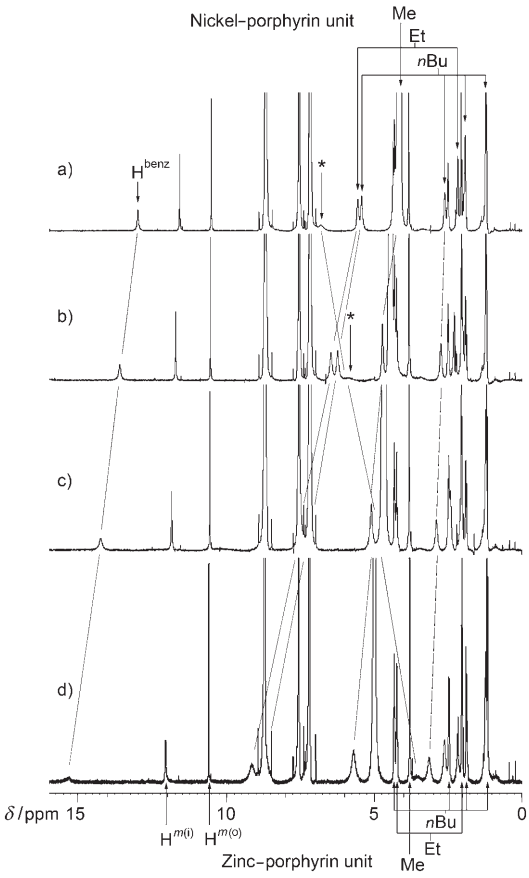


Figure 2. VT-NMR spectra of dimer **13**–NiZn (ca. 1.0 mg in 0.5 mL of C_5D_5N) at a) 80, b) 60, c) 45, and d) 25 °C. Signal assignments for the nickel– and zinc–porphyrin units are shown at the top and bottom, respectively.

of the nickel–porphyrin unit. The other *meso*-proton signals could not be identified.

In the UV/Vis spectra, strong Soret-like bands are seen in the long-wavelength region ($\lambda = 475$ nm for **13**–Zn_2, 484 nm for protonated **13**–H_4, and 470 and 477 nm for **13**–NiZn; Figures 1c, d, and g; solid lines), and moderately strong absorption bands are also observed in the Soret-band region for the monomeric porphyrins (380–420 nm). The most distinctive features of these spectra are the longest-wavelength absorptions of very high intensity in the Q-band region [λ ($\log\varepsilon$) = 656 nm (5.23) for protonated **13**–H_4, 636 nm (5.27) for **13**–Zn_2, and 631 nm (5.21) for **13**–NiZn]. The Q-band absorption of **13**–Zn_2 appears at a shorter wavelength than that of a monocopper complex of a directly fused porphyrin dimer (652 nm).[3b] In the case of **13**–NiZn, the longest-wavelength absorption is also the strongest. Dizinc–porphyrin dimer **13**–Zn_2 and protonated **13**–H_4 show fluorescence with slightly lower energies (by 4 and 7 nm for **13**–Zn_2 and protonated **13**–H_4, respectively) than the longest-wavelength absorptions (Figure 1g, black line: **13**–Zn_2, dark green line: protonated **13**–H_4). Fluorescence was not observed for the benzene-fused dimers **13**–NiZn and **17**.

X-ray analyses of the dimers: Single crystals suitable for X-ray analysis were obtained by the diffusion method. The porphyrin dimer was placed in a small sample tube and dissolved in pyridine, chloroform, or a mixture of chloroform and chlorobenzene. The sample tube was placed in a jar containing methanol or isopropanol. The jar was tightly capped and then left in the dark for an appropriate time ranging from two days to several months. Recrystallization of the benzene-fused porphyrin dimer **13**–Zn_2 from a pyridine/MeOH solvent system gave single crystals containing four molecules of pyridine, two of which were coordinated to the zinc atoms. Two kinds of single crystals of **16** were obtained from PhCl·$CHCl_3$/MeOH (CCM) and PhCl·$CHCl_3$/*i*PrOH (CCI). Both crystals were found to have one-and-a-half molecules of chlorobenzene incorporated in the unit cell. On the other hand, single crystals of **16** obtained from the $CHCl_3$/*i*PrOH (CI) solvent system were found to contain six molecules of chloroform. The crystals of **16**·1.5 PhCl (CCM) and **16**·6 $CHCl_3$ were found to deteriorate when they were left in the original recrystallizing systems. In the CCM crystallizing system, the same single crystals as obtained from the CCI system were gradually formed. The crystal structures were first refined with all solvent molecules present. However, the solvent molecules were not properly modeled due to disorder, and relatively strong electron-density peaks were found near the disordered solvent molecules. Therefore, the core porphyrin dimer structures of **16** were refined without the solvent molecules by means of the SHELX-97 and PLATON SQUEEZE programs.[16] The final crystallographic data are shown in Table 1.

In the two crystal structures of **16**·1.5 PhCl, the solvent molecules occupy rather different positions. Stacking diagrams of **16** are shown in Figure 3. In all of the crystal structures of **16**, the zinc–porphyrin rings are tightly stacked in the *endo* direction forming dimeric structures, and the distances between the zinc–porphyrin rings of **16**·1.5 PhCl(CCM), **16**·1.5 PhCl(CCI), and **16**·6 $CHCl_3$ are 3.380(6), 3.291(6), and 3.281(6) Å, respectively. In the case of **16**·1.5 PhCl(CCM), a weak contact between the zinc–porphyrin rings is observed in the *exo* direction (3.673(7) Å, Figure 3c), while no such contact is observed in the other two structures (Figure 3f and i). The central zinc atoms are offset from the porphyrin rings in the *endo* direction, and are located just above the *meso*-carbon atoms of the other molecules. The zinc–porphyrin rings of **16**·1.5 PhCl show domed out-of-plane distortion, while those of **16**·$CHCl_3$ show ruffled out-of-plane distortion.[17] In contrast to the zinc–porphyrin units, the nickel–porphyrin rings stack in both directions: the *endo* distances in **16**·1.5 PhCl(CCM), **16**·1.5 PhCl(CCI), and **16**·6 $CHCl_3$ are 3.586(7), 3.471(6), and 3.146(8) Å, and the *exo* distances are 3.264(8), 3.200(6), and 3.692(8) Å, respectively (Figure 3b, e, and h). All of the

Table 1. Crystallographic summary.[a]

	16·1.5 PhCl(CCM)	**16**·1.5 PhCl(CCI)	**16**·6 $CHCl_3$	**13**–Zn_2·4 C_5H_5N
M_r	1324.36	1324.36	1903.79	1478.60
formula	$[C_{70}H_{78}N_8NiZn]$	$[C_{70}H_{78}N_8NiZn]$	$[C_{70}H_{78}N_8NiZn]$	$C_{90}H_{98}N_{12}Zn_2$
system	triclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P\bar{1}$
radiation	$Cu_{K\alpha}$	$Mo_{K\alpha}$	$Mo_{K\alpha}$	$Mo_{K\alpha}$
a [Å]	14.1187(15)	11.581(4)	43.739(12)	10.0946(2)
b [Å]	23.316(4)	13.824(4)	14.053(3)	17.1280(4)
c [Å]	11.5019(12)	23.072(9)	31.067(9)	24.2252(11)
α [°]	94.081(14)	73.173(15)	90	77.063(8)
β [°]	113.082(7)	82.513(18)	123.758(4)	88.189(10)
γ [°]	104.185(13)	66.100(13)	90	69.072(7)
V [Å^3]	3317.1(8)	3232.2(19)	15876(7)	3807.5(2)
Z	2	2	8	2
μ [mm^{-1}]	1.745[b]	0.778[b]	1.198[b]	0.686
λ [Å]	1.54178	0.71070	0.71070	0.71070
$2\theta_{max}$	120°	55°	55°	55°
unique reflns	9846	14007	18067	17164
R_{equiv}	0.034 [0.03]	0.049 [0.050]	0.106 [0.100]	0.036
obsd reflns	4238 [4233]	10804 [10122]	9771 [9748]	14050
parameters	[758]	848 [722]	[756]	1021
R_1	[0.0715]	0.1258 [0.0986]	[0.1134]	0.0768
wR_2 (all)	[0.2072]	0.2621 [0.2498]	[0.3436]	0.1331
GOF	[1.020]	1.146 [1.0984]	[1.023]	1.170
T [°C]	23	−190	−180	−100

[a] Values in brackets have been obtained by removal of solvent molecules using the PLATON SQUEEZE program. [b] Values have been calculated based on the molecular formula containing the solvent molecules.

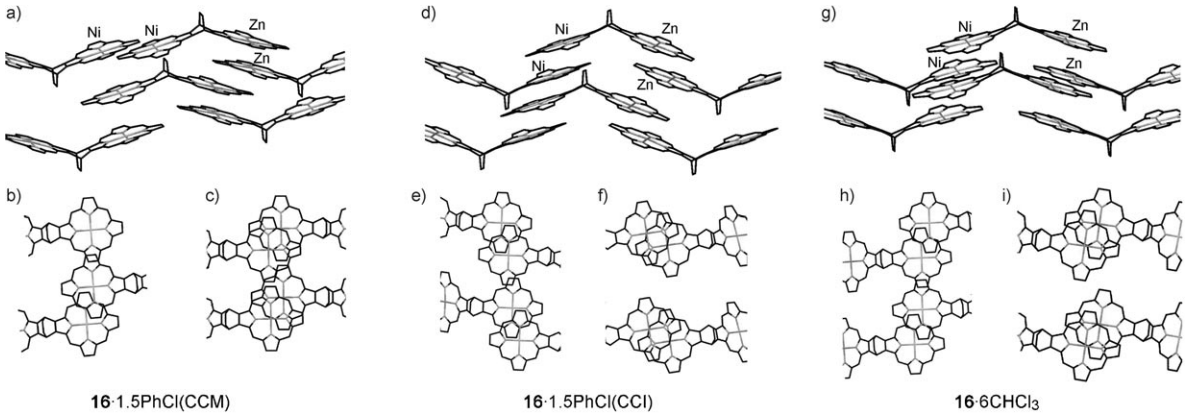


Figure 3. Stacking diagrams of **16**. Peripheral substituents and hydrogen atoms have been omitted for clarity. a) View of six nearest neighbor molecules in **16**·1.5 PhCl(CCM). b) View along the axis perpendicular to the nickel–porphyrin ring of **16**·1.5 PhCl(CCM). c) View along the axis perpendicular to the zinc–porphyrin ring of **16**·1.5 PhCl(CCM). d) View of six nearest neighbor molecules in **16**·1.5 PhCl(CCI). e) View along the axis perpendicular to the nickel–porphyrin ring of **16**·1.5 PhCl(CCI). f) View along the axis perpendicular to the zinc–porphyrin ring of **16**·1.5 PhCl(CCI). g) View of six nearest neighbor molecules in **16**·6 $CHCl_3$. h) View along the axis perpendicular to the nickel–porphyrin ring of **16**·6 $CHCl_3$. i) View along the axis perpendicular to the zinc–porphyrin ring of **16**·6 $CHCl_3$.

nickel–porphyrin rings show saddle-type out-of-plane distortion. The most notable features of the crystal structures are the dihedral angles between the nickel and zinc–porphyrin moieties. These angles are far wider than those of the bicyclo[2.2.2]octadiene-fused dipyrroles:[9a] 148.40(5)°, 137.23(4)°, and 148.82(6)° for **16**·1.5 PhCl(CCM), **16**·1.5 PhCl(CCI), and **16**·6 $CHCl_3$, respectively. This widening is believed to be mainly due to the crystal packing, although rather strong homo-conjugation of the porphyrin π systems may also be a contributing factor.

In the case of **13**–Zn_2·4 C_5H_5N, two crystallographically independent molecules of **13** occupy the special position of −1 symmetry (Figure 4). The dihedral angles between the porphyrin ring and the benzene moiety reflect an almost flat structure (3.84(10) and 1.61(9)°), and intermolecular stacking is not observed due to the coordination of pyridine to the zinc atoms as expected.

Conclusion

We have established a synthetic method for porphyrin dimers fused with a benzene unit based on a retro-Diels–Alder reaction of bicyclo[2.2.2]octadiene in the final step. Advantages of our method are high purity of the product dimers and diversity in the combination of peripheral substituents and central metals. As the final conversion step requires only heat, the dimers could be generated in situ, such as at electrodes. We have also revealed the stacking nature of the nickel–porphyrin unit of the benzene-fused porphyrin dimer by NMR and X-ray analyses. The *endo* space of the bicyclo[2.2.2]octadiene-fused porphyrin dimer has been found to be very wide, while the benzene-fused porphyrin dimer has an almost flat structure.

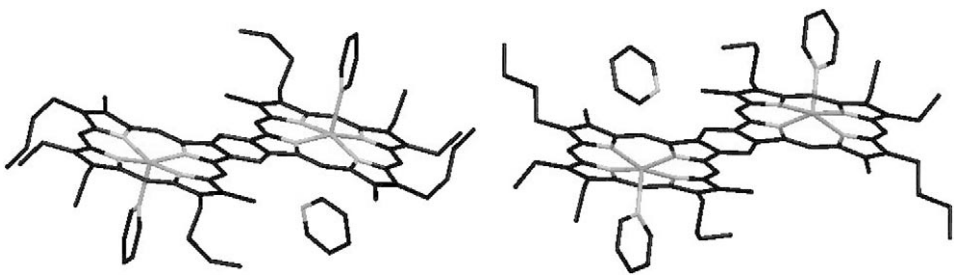


Figure 4. View of crystallographically independent molecules of **13**–Zn_2·4 C_5H_5N along the *a* axis. Hydrogen atoms have been omitted for clarity.

Experimental Section

General: Melting points are uncorrected. Unless otherwise specified, NMR spectra were obtained with a JEOL JNM AL-400 or EX-400 spectrometer at ambient temperature by using $CDCl_3$ as solvent and tetramethylsilane as internal standard for ^1H and ^{13}C. Mass spectra (EI and FAB) were measured with an MStation spectrometer (JEOL MS-700). MALDI-TOF mass spectra were measured on a Voyager DE Pro spectrometer (Applied Biosystems) by using sinapinic acid as the matrix. Elemental analyses were performed on a Yanaco MT-5 elemental analyzer. Preparative GPC was carried out on a JAI LC-9801 chromatograph equipped with JAI-1 H (Φ20×600 mm) and 2.5 H (Φ20×600 mm) columns. THF was distilled from sodium benzophenone ketyl and dichloromethane was distilled from CaH_2 prior to use. DMF was distilled under reduced pressure and then stored over 4 Å MS. Pyridine was distilled from CaH_2 and stored over 4 Å MS. Other dry solvents were purchased from Kanto Chemical Co. Isocyanoacetate esters were prepared according to the literature procedure from the corresponding formamides.[18] 5-Methylpyrrole-2-carboxylates were prepared by the Knorr reaction.

***tert*-Butyl ethyl 4,8-dihydro-4,8-ethano-2*H*,6*H*-benzo[1,2-*c*:4,5-*c*′]dipyrrole-1,5-dicarboxylate and 1,7-dicarboxylate (2b):** An isomeric mixture of ethyl 5- and 6-phenylsulfonyl-4,7-dihydro-4,7-ethano-2*H*-isoindole-

1-carboxylates was prepared according to the literature procedure.[9a] A 1.0 M solution of potassium *tert*-butoxide in THF (3.50 mL, 3.50 mmol) was slowly added to a mixture of the sulfone (1.00 g, 2.80 mmol) and *tert*-butyl isocyanoacetate (0.33 mL, 3.1 mmol) in dry THF (40 mL) at −20 °C under an argon atmosphere. After the addition, the mixture was allowed to warm to room temperature and stirred overnight. The reaction was then quenched by the addition of a 1.0 M hydrochloric acid solution (ca. 20 mL). The resulting mixture was extracted with chloroform. The organic extract was washed with water and brine, dried over sodium sulfate, and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:1) to give a *syn*/*anti* mixture (ca. 1:1) of the title compound (0.96 g, 97 %) as colorless crystals. M.p. 92–94 °C; ^{1}H NMR: δ = 1.38 (t, J = 6.8 Hz, 3H; both isomers), 1.60 (s, 9H; one isomer), 1.61 (s, 9H; other isomer), 1.74–1.69 (m, 4H; both isomers), 4.26 (m, 1H; *syn* isomer), 4.34–4.38 (m, 2H; both isomers), 4.73 (m, 1H; *syn* isomer), 4.76 (m, 2H; *anti* isomer), 5.26 (m, 1H; *syn* isomer), 6.62 (m, 2H; both isomers), 8.36 ppm (br, 2H; both isomers); ^{13}C NMR (all observed peaks are reported; assignments to the individual isomers could not be made): δ = 14.1, 14.6, 14.8, 22.7, 28.2, 28.6, 28.80, 28.82, 29.5, 30.8, 31.10, 31.13, 31.6, 59.87, 59.91, 80.3, 80.4, 112.7, 113.2, 113.3, 113.9, 114.3, 114.9, 115.6, 116.2, 130.6, 130.9, 131.4, 131.8, 134.6, 135.5, 136.7, 161.0, 161.3, 161.6, 161.7 ppm; IR: $\tilde{\nu}_{max}$ = 3320, 2977, 1681, 1415, 1319, 1146 cm^{-1}; MS (EI): m/z (%) = 357 (4) [M^++1], 329 (85) [M^++1−C_2H_4], 272 (100); elemental analysis calcd (%) for $C_{20}H_{24}N_2O_4$·1/4 MeOH·1/4 CH_2Cl_2: C 63.84, H 6.66, N 7.26; found: C 63.47, H 6.60, N 6.99.

4,8-Dihydro-4,8-ethano-2*H*,6*H*-benzo[1,2-*c*:4,5-*c*′]dipyrrole (3): A mixture of diethyl ester **2a**[9a] (0.657 g, 2.00 mmol) and potassium hydroxide (0.65 g) in ethylene glycol (40 mL) was heated at 160 °C for 3.5 h in the dark under an argon atmosphere. After being cooled to room temperature, the mixture was poured onto ice. The resulting mixture was extracted with chloroform. The organic extract was washed with water and brine, dried over sodium sulfate, filtered through a short column of silica gel, and concentrated to give the title compound (0.304 g, 83 %) as a white powder. M.p. > 250 °C; ^{1}H NMR ([D$_6$]DMSO): δ = 1.56 (m, 4H), 4.05 (m, 2H), 6.35 (d, J = 2.4 Hz, 4H), 9.67 ppm (br s, 2H); ^{13}C NMR ([D$_6$]DMSO): δ = 30.3 (two kinds of carbon atom), 107.6, 129.0 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 3378, 2950, 1037, 786 cm^{-1}; MS (EI): m/z (%) = 184 (6) [M^+], 156 (100); elemental analysis calcd (%) for $C_{12}H_{12}N_2$·1/8 H_2O: C 77.29, H 6.62, N 15.02; found: C 77.17, H 6.62, N 15.02.

Benzyl 5-acetoxymethyl-4-*n*-butyl-3-methylpyrrole-2-carboxylate (4a): A solution of sodium nitrite (19.32 g) in water (58 mL) was added over a period of 1 h to a solution of benzyl acetoacetate (48.5 mL, 280 mmol) in acetic acid (56 mL) while the temperature of the mixture was kept below 10 °C by ice cooling. The mixture was then allowed to warm to room temperature and was stirred overnight. Zinc dust (27.1 g, 0.414 g atom) and sodium acetate (33.96 g) were added to a solution of 3-butyl-2,4-pentanedione (12.58 g, 140.0 mmol) in acetic acid (56 mL) at 80 °C, and the temperature was raised to 90 °C. The above benzyl ester mixture was slowly added to this vigorously stirred pentanedione suspension as the reaction temperature was maintained between 90 and 95 °C (ca. 35 min). After 2 h, the reaction mixture was poured into iced water (500 mL) and the solid that separated was collected by filtration. The precipitated solid was thoroughly washed with water and then dissolved in chloroform, to which silica gel was added. After removal of the volatiles in vacuo, the product-adsorbing silica gel was placed on a short column of silica gel and the column was eluted with EtOAc/hexane (30:70). The eluate was concentrated and the residue was recrystallized from ethanol to give benzyl 4-butyl-3,5-dimethylpyrrole-2-carboxylate (33.93 g, 119.0 mmol, 85 %) as colorless needles. M.p. 81 °C; ^{1}H NMR: δ = 0.91 (t, J = 6.8 Hz, 3H), 1.21–1.49 (m, 4H), 2.18 (s, 3H), 2.28 (s, 3H), 2.34 (t, J = 6.8 Hz, 2H), 5.28 (s, 2H), 7.31–7.43 (m, 5H), 8.53 ppm (br s, 1H); ^{13}C NMR: δ = 10.7, 11.4, 14.0, 22.4, 23.7, 33.0, 65.3, 116.3, 122.5, 127.6, 127.9, 128.0, 128.5, 130.0, 136.7, 161.4 ppm; IR: $\tilde{\nu}_{max}$ = 3303, 1662, 1436, 1268 cm^{-1}; MS (EI): m/z = 285 [M^+], 242, 134; elemental analysis calcd (%) for $C_{18}H_{23}NO_2$: C 75.76, H 8.12, N 4.91; found: C 75.79, H 8.09, N 4.92.

Lead tetraacetate (15.38 g, 31.50 mmol) was slowly added to a stirred solution of the benzyl pyrrolecarboxylate (8.56 g, 30.0 mmol) in acetic acid (200 mL) and acetic anhydride (3.1 mL) at room temperature. After 2 h, the mixture was poured into iced water. The precipitate that separated was collected by filtration, washed with water, and dissolved in chloroform. This solution was washed with water, dried over sodium sulfate, and concentrated. The residual solid was triturated with a small amount of hexane to give the title compound (8.93 g, 87 %) as a white powdery solid. M.p. 139 °C; ^{1}H NMR: δ = 0.91 (t, J = 6.8 Hz, 3H), 1.30–1.43 (m, 4H), 2.06 (s, 3H), 2.28 (s, 3H), 2.43 (t, J = 6.8 Hz, 2H), 5.00 (s, 2H), 5.30 (s, 2H), 7.30–7.44 (m, 5H), 9.01 ppm (br s, 1H); ^{13}C NMR: δ = 10.4, 14.0, 20.9, 22.4, 23.5, 33.5, 57.0, 65.7, 118.9, 125.4, 126.7, 127.2, 128.1, 128.1, 128.5, 136.4, 161.1, 171.5 ppm; IR: $\tilde{\nu}_{max}$ = 3305, 1735, 1668, 1276, 1238 cm^{-1}; MS (EI): m/z = 343 [M^+], 300, 284, 135; elemental analysis calcd (%) for $C_{20}H_{25}NO_4$: C 69.95, H 7.34, N 4.08; found: C 69.82, H 7.24, N 4.07.

***tert*-Butyl 5-acetoxymethyl-4-*n*-butyl-3-methylpyrrole-2-carboxylate (4b)**: *tert*-Butyl 4-*n*-butyl-3,5-dimethylpyrrole-2-carboxylate (9.35 g, 31 %) was prepared according to a procedure analogous to that described above, using *tert*-butyl acetoacetate (47.4 mL, 210 mmol) instead of benzyl acetoacetate. The product was obtained as colorless needles. M.p. 94–95 °C; ^{1}H NMR: δ = 0.91 (t, J = 7.3 Hz, 3H), 1.33–1.40 (m, 4H), 1.59 (s, 9H), 2.18 (s, 3H), 2.24 (s, 3H), 2.34 (t, 2H, J = 7.3 Hz), 8.41 ppm (br s, 1H); ^{13}C NMR: δ = 10.6, 11.5, 14.0, 22.5, 23.7, 28.6, 33.1, 79.9, 117.9, 122.1, 126.1, 128.7, 161.4 ppm; IR: $\tilde{\nu}_{max}$ = 3323, 2951, 2927, 2868, 1664, 1279, 1161, 1088 cm^{-1}; MS (EI): m/z (%) = 251 (28) [M^+], 195 (36), 178 (9), 152 (100); elemental analysis calcd (%) for $C_{15}H_{25}NO_2$: C 71.67, H 10.02, N 5.57; found: C 71.50, H 9.81, N 5.63.

Acetoxylation of *tert*-butyl 4-*n*-butyl-3,5-dimethylpyrrole-2-carboxylate (1.26 g, 5.00 mmol) by the method described above gave the title compound (1.21 g, 78 %) as colorless crystals. M.p. 85 °C; ^{1}H NMR: δ = 0.91 (t, J = 7.3 Hz, 3H), 1.31–1.36 (m, 4H), 1.56 (s, 9H), 2.07 (s, 3H), 2.24 (s, 3H), 2.42 (t, J = 7.3 Hz, 2H), 5.00 (s, 2H), 8.41 ppm (br s, 1H); ^{13}C NMR: δ = 10.4, 13.8, 20.9, 22.3, 23.6, 28.3, 33.6, 57.1, 80.6, 120.5, 125.2, 125.3, 126.1, 161.0, 171.5 ppm; IR: $\tilde{\nu}_{max}$ = 3309, 2976, 2956, 2931, 2860, 1736, 1660 cm^{-1}; MS (EI): m/z (%) = 309 (10) [M^+], 281 (41), 225 (100), 210 (32), 182 (83); elemental analysis calcd (%) for $C_{17}H_{27}NO_4$: C 65.99, H 8.80, N 4.53; found: C 65.87, H 8.66, N 4.52.

Ethyl 5-hydroxymethyl-3,4-diethylpyrrole-2-carboxylate (4c): Phosphoryl chloride (16.8 mL, 180 mmol) was slowly added to DMF (2.33 mL, 30.0 mmol) at 0 °C. After being stirred for 15 min at room temperature, the mixture was diluted with dry 1,2-dichloroethane (100 mL). A solution of ethyl 3,4-diethylpyrrole-2-carboxylate[13] (1.95 g, 10 mmol) in dry 1,2-dichloroethane (50 mL) was then added and the resulting mixture was refluxed for 2 h. Thereafter, an aqueous solution of sodium acetate (73.8 g in 200 mL) was slowly added to quench the reaction, and the resulting mixture was refluxed for 15 min in order to decompose the iminium intermediate. After being cooled to room temperature, the mixture was diluted with water and then extracted with chloroform. The organic extract was washed with water, saturated sodium hydrogencarbonate solution, and brine, dried over sodium sulfate, and concentrated. The residue was purified by column chromatography on silica gel to give ethyl 5-formyl-3,4-diethylpyrrole-2-carboxylate (2.12 g, 95 %) as colorless crystals. M.p. 52 °C; ^{1}H NMR: δ = 1.16 (t, J = 7.3 Hz, 3H), 1.24 (t, J = 7.5 Hz, 3H), 1.38 (t, J = 7.3 Hz, 3H), 2.71–2.79 (m, 4H), 4.36 (q, J = 7.3 Hz, 2H), 9.58 (br s, 1H), 9.78 ppm (s, 1H); ^{13}C NMR: δ = 12.3, 15.6, 16.6, 17.5, 60.9, 124.1, 129.4, 133.0, 136.3, 160.6, 179.2 ppm; IR: $\tilde{\nu}_{max}$ = 3268, 2964, 2929, 2869, 2811, 1693, 1666, 1481, 1255 cm^{-1}; MS (EI): m/z (%) = 223 (100) [M^+], 194 (62), 176 (43), 162 (35); elemental analysis calcd (%) for $C_{12}H_{17}NO_3$: C 64.55, H 7.67, N 6.27; found: C 64.47, H 7.48, N 6.26.

The formylpyrrole (1.88 g, 8.42 mmol) was dissolved in dry THF/EtOH (50 mL/12.5 mL) and $CeCl_3$·7 H_2O (3.14 g, 8.42 mmol) was added. Sodium borohydride (0.330 g, 8.42 mmol) was then added in three portions to the mixture at 0 °C. After 1 h, water was added and the precipitate was removed by filtration. The filtrate was extracted with ethyl acetate. The organic extract was washed with brine, dried over sodium sulfate, and concentrated to give the title compound as a viscous oil, which was used without further purification. ^{1}H NMR: δ = 1.09 (t, J = 6.7 Hz, 3H), 1.15 (t, J = 6.7 Hz, 3H), 1.36 (t, J = 6.7 Hz, 3H), 1.93 (br s, 1H), 2.43 (q, J = 6.7 Hz, 2H), 2.73 (q, J = 6.7 Hz, 2H), 4.31 (q, J = 6.7 Hz, 2H), 4.65 (s, 2H), 9.12 ppm (br s, 1H).

Bis(dipyrromethane) 6: *p*-TSA·H_2O (0.15 g) was added to a solution of the *syn*-dipyrrole *syn*-**2a** (0.657 g, 2.00 mmol) and *tert*-butyl 5-(acetoxymethyl)pyrrole-2-carboxylate **4b** (1.86 g, 6.00 mmol) in acetic acid (60 mL) and the mixture was stirred for 2 h at room temperature. Water was then added and the resulting mixture was extracted with ethyl acetate. The organic extract was successively washed with saturated sodium hydrogencarbonate solution, water, and brine, dried over sodium sulfate, and concentrated. The residue was purified by column chromatography on silica gel to give the title compound (0.68 g, 41%) as a colorless powder. M.p. 161°C (decomp); ^{1}H NMR: $\delta=0.88$ (t, $J=6.8$ Hz, 6H), 1.27 (m, 8H), 1.36 (t, $J=7.3$ Hz, 6H), 1.48 (s, 18H), 1.72–1.80 (m, 4H), 2.25 (s, 6H), 2.35 (t, $J=7.3$ Hz, 4H), 3.62 (m, 1H), 3.85 (s, 4H), 4.30 (q, $J=6.8$ Hz, 2H), 5.19 (m, 1H), 8.87 (brs, 2H), 8.94 ppm (brs, 2H); ^{13}C NMR: $\delta=10.7$, 14.0, 14.5, 22.6, 23.1, 23.8, 27.8, 28.4, 28.7, 29.1, 31.9, 33.4, 60.0, 80.2, 113.6, 119.0, 122.5, 124.6, 126.2, 128.6, 128.6, 136.5, 161.3, 162.3 ppm; IR: $\tilde{\nu}_{max}=3448$, 3316, 2931, 1697, 1658, 1446 cm^{-1}; MS (FAB$^+$): $m/z=827$ [M^++1]; elemental analysis calcd (%) for $C_{48}H_{66}N_4O_8$: C 69.71, H 8.47, N 6.77; found: C 69.88, H 8.39, N 6.48.

Dipyrromethane dicarbaldehyde 7: Ethyl 3,4-diethylpyrrole-2-carboxylate[13] (5.17 g, 26.5 mmol), dimethoxymethane (5.89 mL, 66.3 mmol), and *p*-TSA·H_2O (0.30 g) were dissolved in ethanol (50 mL) and the solution was refluxed overnight under nitrogen. Thereafter, water was added to quench the reaction, and the resulting mixture was extracted with chloroform. The organic extract was washed with water and brine, dried over sodium sulfate, and concentrated. The residue was purified by column chromatography on silica gel to give diethyl dipyrromethane dicarboxylate (5.03 g, 94%) as colorless crystals. M.p. 104°C; ^{1}H NMR: $\delta=1.06$ (t, $J=7.3$ Hz, 6H), 1.15 (t, $J=7.3$ Hz, 6H), 1.28 (t, $J=6.8$ Hz, 3H), 2.42 (q, $J=7.3$ Hz, 4H), 2.71 (q, $J=7.3$ Hz, 4H), 3.89 (s, 2H), 4.23 (q, $J=6.8$ Hz, 4H), 9.30 ppm (brs, 2H); ^{13}C NMR: $\delta=14.3$, 15.8, 16.1, 17.1, 18.4, 22.9, 59.8, 117.1, 123.3, 129.4, 133.7, 161.8 ppm; IR: $\tilde{\nu}_{max}=3336$, 2985, 1697, 1654, 1444, 1263 cm^{-1}; MS (EI): m/z (%) = 402 (34) [M^+], 207 (100); elemental analysis calcd (%) for $C_{23}H_{34}N_2O_4$: C 68.63, H 8.51, N 6.96; found: C 68.61, H 8.50, N 6.80.

The dipyrromethane dicarboxylate (2.25 g, 5.60 mmol), potassium hydroxide (3.16 g), and ethylene glycol (100 mL) were placed in a flask, which was then flushed with argon and protected from light. The mixture was stirred at 160°C for 2.5 h. It was then diluted with water and extracted with ethyl acetate. The organic extract was washed with saturated sodium hydrogencarbonate solution, water, and brine, dried over sodium sulfate, and concentrated to give the crude dipyrromethane, which was used in the next step without further purification.

Phosphoryl chloride (3.33 mL) was slowly added to DMF (2.62 mL) at 0°C. The mixture was stirred for 15 min at room temperature and then diluted with dry dichloromethane (15 mL). A solution of the above crude dipyrromethane in dry dichloromethane (10 mL) was then added and the mixture was refluxed for 45 min. An aqueous solution of sodium acetate (14.6 g in 50 mL) was slowly added to quench the reaction and then the resulting mixture was refluxed for 1 h in order to decompose an iminium intermediate. Thereafter, the mixture was cooled to room temperature, diluted with water, and extracted with chloroform. The organic extract was washed with water, saturated sodium hydrogencarbonate solution, and brine, dried over sodium sulfate, and concentrated. The residue was purified by column chromatography on silica gel to give the title compound as a brownish powder. M.p. 189°C; ^{1}H NMR: $\delta=1.08$ (t, $J=7.3$ Hz, 6H), 1.24 (t, $J=7.3$ Hz, 6H), 2.45 (q, $J=7.3$ Hz, 4H), 2.71 (q, $J=7.3$ Hz, 4H), 3.99 (s, 2H), 9.52 (s, 2H), 11.16 ppm (brs, 2H); ^{13}C NMR: $\delta=15.9$, 16.9, 17.2, 17.7, 22.7, 124.1, 128.0, 135.1, 139.2, 176.8 ppm; IR: $\tilde{\nu}_{max}=3224$, 2962, 1644, 1616, 1440, 1240 cm^{-1}; MS (EI): m/z (%) = 314 (70) [M^+], 285 (56), 163 (100); elemental analysis calcd (%) for $C_{19}H_{26}N_2O_2$: C 72.58, H 8.33, N 8.91; found: C 72.30, H 8.23, N 8.87.

Dibenzyl tripyrrane dicarboxylate 10a:[19] 3,4-Diethylpyrrole (**9**)[13] (1.30 g, 10.5 mmol) and benzyl 5-acetoxymethyl-4-*n*-butyl-3-methylpyrrole-2-carboxylate (**4a**) (7.21 g, 21.0 mmol) were dissolved in a mixture of acetic acid (10 mL) and ethanol (150 mL). The solution was refluxed for 18 h in the dark and then allowed to cool to room temperature. Further ethanol (50 mL) was added and the resulting mixture was left at 0°C for 5 h. The precipitate that formed was collected by filtration and washed with ethanol to give the title compound as colorless crystals. M.p. 202°C; ^{1}H NMR: $\delta=0.84$ (t, $J=6.8$ Hz, 6H), 1.15 (t, $J=7.3$ Hz, 6H), 1.27–1.30 (m, 8H), 2.23 (s, 6H), 2.28 (m, 4H), 2.48 (q, $J=7.3$ Hz, 4H), 3.54 (s, 4H), 4.34 (s, 4H), 6.97 (m, 4H), 7.20–7.23 (m, 6H), 8.77 (brs, 1H), 11.22 ppm (brs, 2H); ^{13}C NMR: $\delta=11.1$, 13.9, 16.9, 17.8, 22.1, 22.8, 23.9, 33.5, 65.2, 117.1, 118.6, 121.6, 122.4, 126.5, 126.6, 127.1, 128.0, 133.4, 137.1, 162.7 ppm; IR: $\tilde{\nu}_{max}=3424$, 3297, 2958, 2927, 2857, 1658, 1454, 1272 cm^{-1}; MS (FAB$^+$): $m/z=689$ [M^+]; elemental analysis calcd (%) for $C_{44}H_{55}N_3O_4$: C 76.60, H 8.04, N 6.09; found: C 76.36, H 8.10, N 5.86.

All-ethyl tripyrrane dicarboxylate 10b: 3,4-Diethylpyrrole (**9**)[13] (0.49 g, 4.0 mmol), ethyl 5-acetoxymethyl-3,4-diethylpyrrole-2-carboxylate (**4c**) (1.80 g, 8.00 mmol), and *p*-TSA·H_2O (0.14 g, 0.80 mmol) were dissolved in ethanol (140 mL). The solution was refluxed overnight in the dark. It was then cooled to room temperature and concentrated to a volume of about 50 mL in vacuo. Water was added and the resulting mixture was extracted with ethyl acetate. The organic extract was washed with water and brine, dried over sodium sulfate, and concentrated. The residue was purified by column chromatography on silica gel to give the title compound **10b** as yellow crystals. M.p. 173–175°C; ^{1}H NMR: $\delta=0.61$ (m, 24H), 2.44 (m, 8H), 2.63 (q, $J=7.3$ Hz, 4H), 3.32 (q, $J=7.3$ Hz, 4H), 3.76 (s, 4H), 9.11 (brs, 1H), 11.01 ppm (brs, 2H); ^{13}C NMR: $\delta=13.9$, 16.0, 16.5, 16.6, 17.0, 17.7, 18.6, 22.2, 59.7, 117.0, 118.5, 122.1, 122.4, 131.9, 132.4, 162.6 ppm; IR: $\tilde{\nu}_{max}=3384$, 3288, 2962, 1651, 1281 cm^{-1}; MS (EI): $m/z=537$ [M^+], 491, 313, 207; HRMS (EI): calcd for $C_{32}H_{47}N_3O_4$: 537.3567; found: 537.3536.

Tripyrrane dicarbaldehyde 11a: Palladium on charcoal (10%, 0.50 g) was placed in a two-necked flask, one neck of which was fitted with a three-way stopcock connected to a hydrogen balloon and a water aspirator, while the other neck was fitted with a rubber septum. Freshly distilled THF (20 mL) was introduced through the septum by means of a syringe. The suspension was vigorously stirred and the three-way stopcock was opened to the water aspirator. As soon as bubbling occurred, hydrogen was flushed into the flask. This manipulation was repeated three times to activate the catalyst. Then, a solution of the dibenzyl diester **10a** (2.09 g, 3.03 mmol) in freshly distilled THF (30 mL) was added to the vigorously stirred suspension by means of a syringe at room temperature. The mixture was stirred overnight under a hydrogen atmosphere. The suspension was then filtered through a Celite pad, which was thoroughly washed with ethyl acetate. The filtrate was concentrated in vacuo and flushed with argon. The residue was cooled in an ice-bath and then treated with trifluoroacetic acid (5 mL) under argon. Trimethyl orthoformate (10 mL) was slowly added to the solution at 0°C and the resulting mixture was stirred for 1 h at the same temperature. Still at 0°C, a 1 M solution of sodium hydroxide in 50% aqueous methanol was added to neutralize the solution. The resulting mixture was poured into iced water (200 mL). The precipitated solid was collected by filtration, washed with water, and rinsed with hexane. The title compound was obtained in 81% yield (1.178 g) as a pink powder. M.p. 208°C; ^{1}H NMR: $\delta=0.91$ (t, $J=7.3$ Hz, 6H), 1.09 (t, $J=7.3$ Hz, 6H), 1.34 (m, 8H), 2.21 (s, 6H), 2.36–2.44 (m, 8H), 3.82 (s, 4H), 8.78 (brs, 1H), 9.20 (s, 2H), 9.84 ppm (brs, 2H); ^{13}C NMR: $\delta=8.9$, 13.9, 16.6, 17.7, 22.6, 22.7, 23.5, 32.9, 120.6, 121.6, 123.2, 128.0, 133.0, 138.4, 175.3 ppm; IR: $\tilde{\nu}_{max}=3251$, 2958, 1639, 1446 cm^{-1}; MS (FAB$^+$): $m/z=476$ [M^+−1]; elemental analysis calcd (%) for $C_{30}H_{43}N_3O_2$: C 75.43, H 9.07, N 8.80; found: C 75.28, H 9.00, N 8.58.

All-ethyl tripyrrane dicarbaldehyde 11b: All-ethyl tripyrrane dicarboxylate diethyl diester **10b** (0.58 g, 1.08 mmol) and LiOH·H_2O (0.27 g, 6.4 mmol) were dissolved in a mixture of freshly distilled THF (18 mL), ethanol (7 mL), and water (7 mL) under a nitrogen atmosphere. The mixture was heated at 80°C for 1 h. Two further portions of LiOH·H_2O (0.27 g, 6.4 mmol) were added at intervals of 1 h. The consumption of **10b** and its mono ester was verified by TLC. The mixture was then cooled to room temperature and acidified to pH 2–3 by the addition of 1% hydrochloric acid. The acidified mixture was extracted with ethyl acetate. The organic extract was washed with brine, dried over sodium sulfate, and concentrated to leave the corresponding dicarboxylic acid as a solid. The flask containing the solid was flushed with argon and cooled in ice. Trifluoroacetic acid (1.8 mL) was added and the resulting mixture was stirred for 10 min. Trimethyl orthoformate (3.6 mL) was then slowly

added to the solution at 0 °C and the resulting mixture was stirred for 1 h at the same temperature. Still at 0 °C, a 1 M solution of sodium hydroxide in 50% aqueous methanol was added to neutralize the solution. The resulting mixture was poured into iced water (100 mL). The precipitated solid was collected by filtration, washed with water, and rinsed with hexane to give the title compound (0.055 g, 11%) as a purple powder. A further crop (0.250 g, 51%) was obtained by chromatographic purification of the hexane washing. M.p. 148–151 °C; ^{1}H NMR: δ = 1.04 (m, 18H), 2.42 (m, 8H), 2.58 (q, J = 7.6 Hz, 4H), 3.82 (s, 4H), 9.08 (s, 2H), 9.49 (br s, 1H), 10.26 ppm (br s, 2H); ^{13}C NMR: δ = 15.8, 16.5, 16.8, 17.1, 17.6, 17.7, 22.6, 120.7, 121.4, 123.8, 127.3, 138.3, 139.8, 175.7 ppm; IR: $\tilde{\nu}_{max}$ = 3269, 2962, 1624, 1441 cm^{-1}; MS (EI): m/z = 449 [M^+], 285, 269, 163; HRMS (EI): calcd for $C_{28}H_{39}N_3O_2$: 449.3042; found: 449.3039.

Free-base porphyrin fused with ethyl pyrrole-2-carboxylate through a bicyclo[2.2.2]octadiene unit (14-H$_2$): Trifluoroacetic acid (2 mL) was added to a diastereomeric mixture of dipyrrole **2b** (0.356 g, 1 mmol) under an argon atmosphere and the mixture was stirred for 10 min at room temperature. It was then diluted with dry dichloromethane (64 mL), tripyrrane dicarbaldehyde **11a** was added, and the resulting mixture was stirred for 1 day. Thereafter, triethylamine (2 mL) and DDQ (0.146 g) were added, and the mixture was further stirred overnight. It was then washed with saturated sodium hydrogencarbonate solution, water, and brine, dried over sodium sulfate, and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/CHCl$_3$, 5:95) to give a dark-red solid. Recrystallization from CHCl$_3$/MeOH gave the title compound (0.188 g, 27%) as red crystals. M.p. 192 °C (decomp); ^{1}H NMR: δ = −3.89 (br s, 2H), 1.11 (t, J = 7.3 Hz, 6H), 1.66 (t, J = 7.3 Hz, 3H), 1.75 (m, 4H), 1.92 (t, J = 7.3 Hz, 6H), 2.18 (m, 2H), 2.28 (m, 4H), 2.37 (m, 2H), 3.63 (s, 3H), 3.63 (s, 3H), 4.02–4.13 (m, 8H), 4.48–4.60 (m, 2H), 6.02 (s, 1H), 6.55 (s, 1H), 6.95 (d, J = 2.4 Hz, 1H), 8.41 (br s, 1H), 10.08 (s, 2H), 10.20 (s, 1H), 10.26 ppm (s, 1H); ^{13}C NMR (some signals could not be observed owing to broadening due to tautomerism and some signal overlap): δ = 11.7, 11.8, 14.2, 14.8, 18.3, 19.8, 23.1, 26.3, 29.8, 30.5, 33.5, 33.7, 35.4, 96.25, 96.27, 97.2, 97.3, 133.2, 136.4, 136.5, 138.2, 141.0, 141.5, 142.2, 146.9, 147.3, 148.0, 161.7 ppm; UV/Vis (CHCl$_3$): λ_{max} (log ε) = 400 (5.18), 498 (4.14), 530 (3.88), 569 (3.82), 621 nm (3.65); MS (MALDI-TOF): m/z = 696.79 [M^++1]; HRMS (FAB$^+$): calcd for $C_{45}H_{54}N_5O_2$+H$^+$: 696.4275; found: 696.4283.

Zinc–porphyrin fused with ethyl pyrrole-2-carboxylate through a bicyclo[2.2.2]octadiene unit (14–Zn): A solution of the free-base porphyrin **14**-H$_2$ (0.139 g, 0.20 mmol) and zinc acetate dihydrate (0.65 g, 3.0 mmol) in chloroform (90 mL) was stirred overnight under an argon atmosphere. The mixture was then washed with water and brine, dried over sodium sulfate, and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/CHCl$_3$, 5:95) to give the zinc–porphyrin (0.149 g, 98%) as red crystals. M.p. 194 °C (decomp); ^{1}H NMR: δ = 1.06 (t, J = 7.3 Hz, 6H), 1.67–1.78 (m, 7H), 1.83 (t, J = 7.6 Hz, 3H), 2.22 (m, 4H), 2.23 (m, 2H), 2.44 (m, 2H), 3.65 (s, 3H), 3.66 (s, 3H), 3.96 (m, 4H), 4.54 (m, 2H), 6.07 (s, 1H), 6.57 (s, 1H), 7.03 (d, J = 2.4 Hz, 1H), 8.35 (br s, 1H), 9.43 (s, 2H), 10.12 (s, 1H), 10.20 ppm (s, 1H); ^{13}C NMR (some signals could not be found due to overlap): δ = 11.8, 11.8, 14.3, 14.9, 18.5, 19.5, 19.5, 23.0, 26.0, 29.9, 30.6, 33.6, 33.9, 35.4, 35.4, 60.2, 96.5, 97.9, 113.8, 115.0, 133.49, 135.96, 136.03, 141.0, 141.1, 141.4, 141.6, 141.7, 146.7, 147.5, 149.5, 147.6, 147.8, 147.9, 148.7, 161.6 ppm; UV/Vis (CHCl$_3$): λ_{max} (log ε) = 403 (5.49), 532 (4.19), 570 nm (4.24); MS (MALDI-TOF): m/z = 757.74 [M^++1]; HRMS (FAB$^+$): calcd for $C_{45}H_{51}N_5O_2Zn$+H$^+$: 758.3413; found: 758.3427.

Nickel–porphyrin fused with ethyl pyrrole-2-carboxylate through a bicyclo[2.2.2]octadiene unit (14–Ni): A solution of the free-base porphyrin **14**-H$_2$ (70 mg, 0.10 mmol) and nickel(II) acetate (370 mg, 1.5 mmol) in chloroform (90 mL) was refluxed overnight under an argon atmosphere. Thereafter, it was filtered, and the filtrate was washed with saturated sodium hydrogencarbonate solution and brine, dried over sodium sulfate, and concentrated. The residue was purified by column chromatography on silica gel (CHCl$_3$) to give the nickel–porphyrin (64 mg, 85%) as red crystals. M.p. 200 °C (decomp); ^{1}H NMR: δ = 1.07 (t, J = 7.3 Hz, 3H), 1.08 (t, J = 7.3 Hz, 3H), 1.63 (t, J = 7.1 Hz, 3H), 1.68 (m, 4H), 1.81 (t, J = 7.7 Hz, 6H), 2.16 (m, 6H), 2.32 (m, 2H), 3.49 (s, 3H), 3.50 (s, 3H), 3.83–3.95 (m, 8H), 4.51 (m, 2H), 5.84 (s, 1H), 6.37 (s, 1H), 6.91 (d, J = 2.4 Hz, 1H), 8.40 (br s, 1H), 9.74 (s, 1H), 9.74 (s, 1H), 9.88 (s, 1H), 9.94 ppm (s, 1H); ^{13}C NMR (some signals could not be found due to overlap): δ = 11.7, 11.8, 14.3, 14.9, 18.3, 19.8, 23.03, 23.05, 26.2, 29.7, 30.5, 33.3, 33.6, 35.3, 60.1, 96.6, 97.4, 97.5, 113.7, 114.9, 132.9, 134.8, 135.0, 136.65, 136.71, 140.60, 140.63, 141.0, 141.1, 141.3, 141.4, 141.68, 141.7, 142.6, 148.4, 149.3, 161.6 ppm; UV/Vis (CHCl$_3$): λ_{max} (log ε) = 394 (5.28), 516 (4.04), 554 nm (4.37); MS (MALDI-TOF): m/z = 752.73 [M^++1]; HRMS (FAB$^+$): calcd for $C_{45}H_{51}N_5O_2Ni$+H$^+$: 752.3474; found: 752.3532.

Nickel–porphyrin fused with pyrrole through a bicyclo[2.2.2]octadiene unit (15): A mixture of **14**–Ni (75 mg, 0.10 mmol) and potassium hydroxide (3.4 g) in ethylene glycol (70 mL) was heated at 180 °C for 2 h in the dark under an argon atmosphere. It was then diluted with water at room temperature and the resulting mixture was extracted with ethyl acetate. The organic extract was washed with saturated sodium hydrogencarbonate solution, water, and brine, dried over sodium sulfate, and concentrated. The residue was purified by column chromatography on silica gel (CHCl$_3$) to give the title compound (56 mg, 82%) as red crystals. M.p. 210 °C (decomp); ^{1}H NMR: δ = 0.98 (t, 6H, J = 7.3 Hz), 1.58 (m, 4H), 1.71 (t, J = 7.6 Hz, 6H), 2.07 (m, 6H), 2.25 (m, 2H), 3.39 (s, 6H), 3.73–3.82 (m, 8H), 5.74 (s, 2H), 6.65 (d, J = 2.2 Hz, 2H), 7.34 (br s, 1H), 9.64 (s, 2H), 9.81 ppm (s, 2H); ^{13}C NMR: δ = 11.8, 14.3, 18.4, 19.8, 23.1, 26.3, 31.0, 33.2, 35.3, 96.5, 97.5, 109.0, 130.6, 135.2, 136.6, 140.5, 141.1, 141.2, 141.6, 142.5, 149.7 ppm; UV/Vis (CHCl$_3$): λ_{max} (log ε) = 393 (5.27), 516 (4.02), 553 nm (4.37); MS (MALDI-TOF): m/z = 680.76 [M^++1]; HRMS (FAB$^+$): calcd for $C_{42}H_{47}N_5Ni$+H$^+$: 680.3263; found: 680.3221.

Symmetric zinc–porphyrin dimer fused with a bicyclo[2.2.2]octadiene unit (12–Zn$_2$): Trifluoroacetic acid (6.08 mL) was added to a stirred solution of dipyrrole **3** (93 mg, 0.51 mmol) and tripyrrane dicarbaldehyde **11a**[10d] (483 mg, 1.01 mmol) in chloroform (115 mL) in the dark under a nitrogen atmosphere. After stirring the mixture at 50 °C for 18 h, triethylamine (10.7 mL) was slowly added at room temperature. The resulting mixture was washed with water and dried over sodium sulfate. Zinc acetate dihydrate (264 mg) was then added and the resulting mixture was stirred at room temperature for 22 h. It was then washed with water and brine, dried over sodium sulfate, and concentrated. The residue was purified by column chromatography on silica gel (CHCl$_3$/hexane, 1:1) to give the title compound (125 mg, 21%) as red crystals. M.p. > 160 °C (decomp); ^{1}H NMR: δ = 1.10 (t, 12H, J = 7.3 Hz), 1.73 (m, 8H), 1.84 (t, J = 7.3 Hz, 12H), 2.28 (m, 8H), 2.88 (m, 4H), 3.93 (s, 12H), 4.0–4.1 (m, 16H), 7.88 (m, 2H), 10.01 (s, 4H), 10.83 ppm (s, 4H); ^{13}C NMR: δ = 12.2, 14.2, 18.5, 19.8, 23.1, 26.3, 31.8, 35.4, 36.5, 97.1, 98.6, 136.6, 141.5, 142.1, 142.3, 147.5, 148.3, 148.5, 151.5 ppm; UV/Vis (CHCl$_3$): λ_{max} (log ε) = 399 (5.65), 414 (5.65), 533 (4.65), 574 nm (4.74); MS (FAB+): m/z = 1162 [M^+−C$_2$H$_4$]; elemental analysis calcd (%) for $C_{72}H_{82}N_8Zn_2$: C 72.65, H 6.94, N 9.41; found: C 72.36, H 7.03, N 9.23.

Symmetric free-base porphyrin dimer fused with a bicyclo[2.2.2]octadiene unit (12-H$_4$): Trifluoroacetic acid (4 mL) was added to a stirred solution of zinc–porphyrin dimer **12**–Zn$_2$ (43 mg, 0.036 mmol) in chloroform (5 mL) in the dark under a nitrogen atmosphere. After 1 h, the mixture was washed with water, dried over sodium sulfate, and concentrated. The residue was purified by column chromatography on silica gel (CHCl$_3$) to give the title compound (38 mg, 99%) as a red powder. M.p. > 170 °C (decomp); ^{1}H NMR: δ = −3.79 (br s, 4H), 1.13 (t, J = 6.8 Hz, 12H), 1.78 (m, 8H), 1.93 (t, J = 7.3 Hz, 12H), 2.33 (m, 8H), 2.77 (m, 4H), 3.91 (s, 12H), 4.10–4.16 (m, 16H), 7.84 (m, 2H), 10.14 (s, 4H), 10.79 ppm (s, 4H); ^{13}C NMR: δ = 12.2, 13.8, 17.4, 20.1, 22.9, 26.6, 29.7, 34.3, 36.5, 98.0, 100.1, 136.0, 138.4, 140.2, 142.3, 142.7, 142.7, 143.6, 148.1 ppm; UV/Vis (CHCl$_3$): λ_{max} (log ε) = 397 (5.30), 409 (5.29), 500 (4.49), 536 (4.27), 567 (4.16), 622 nm (4.02); UV/Vis (1% TFA in CHCl$_3$): λ_{max} (log ε) = 400 (5.64), 419 (5.74), 550 (4.60), 597 nm (4.29); MS (MALDI-TOF): m/z = 1064.1 [M^++1]; elemental analysis calcd (%) for $C_{72}H_{86}N_8$·8/5 CHCl$_3$: C 70.46, H 7.04, N 8.93; found: C 70.52, H 7.12, N 9.00.

Nickel and zinc–porphyrin dimer fused with a bicyclo[2.2.2]octadiene unit (12–NiZn): Trifluoroacetic acid (0.5 mL) was added to a stirred solution of pyrrole-fused nickel–porphyrin **15** (54 mg, 0.079 mmol) and tripyrrane dicarbaldehyde **11a**[10d] (38 mg, 0.079 mmol) in dichloromethane

(24 mL) in the dark under a nitrogen atmosphere. After 18 h, triethylamine (0.5 mL) was slowly added at room temperature, followed by DDQ (36 mg) and zinc acetate dihydrate (300 mg), and the resulting mixture was stirred at room temperature overnight. It was then washed with saturated sodium hydrogencarbonate solution, water, and brine, dried over sodium sulfate, and concentrated. The residue was purified by column chromatography on silica gel ($CHCl_3$) to give the crude product. Recrystallization from $CHCl_3$/MeOH gave the title compound (11 mg, 12%) as red crystals. M.p. > 160 °C (decomp); ^{1}H NMR: $\delta = 0.91$ (t, $J = 7.4$ Hz, 6H), 1.08 (t, $J = 7.3$ Hz, 6H), 1.47 (m, 4H), 1.50 (t, $J = 7.6$ Hz, 6H), 1.70 (m, 4H), 1.78 (t, $J = 7.5$ Hz, 6H), 1.97 (m, 4H), 2.19 (m, 4H), 2.81 (m, 4H), 3.60–3.73 (m, 8H), 3.73 (s, 6H), 3.80 (s, 6H), 3.80–3.98 (m, 8H), 7.70 (m, 2H), 9.31 (s, 2H), 9.72 (s, 2H), 10.55 (s, 2H), 10.56 ppm (s, 2H); UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$) = 394 (5.42), 410 (5.49), 535 (4.40), 555 (4.53), 572 nm (4.50); MS (MALDI-TOF): $m/z = 1154.96$ [M^+(^{60}Ni)+1]; HRMS (FAB$^+$): calcd for $C_{72}H_{82}N_8NiZn+H^+$: 1181.5385; found: 1181.5432.

Asymmetric dimer 16: Dimer **16** was prepared in 35% yield according to the procedure described above using **11b** instead of **11a**. It was obtained as red crystals; m.p. > 155 °C (decomp); ^{1}H NMR: $\delta = 1.07$ (t, $J = 7.3$ Hz, 6H), 1.66–1.75 (m, 4H), 1.79 (t, $J = 7.6$ Hz, 6H), 1.81 (t, $J = 7.6$ Hz, 6H), 1.90 (t, $J = 7.6$ Hz, 6H), 2.13 (t, $J = 7.6$ Hz, 6H), 2.19 (m, 4H), 2.84 (m, 4H), 3.76 (s, 6H), 3.92 (m, 8H), 3.99 (q, $J = 7.6$ Hz, 4H), 4.08 (q, $J = 7.6$ Hz, 4H), 4.35 (m, 4H), 7.69 (m, 2H), 9.75 (s, 2H), 9.98 (s, 2H), 10.49 (s, 2H), 10.72 ppm (s, 2H); UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$) = 394 (5.44), 410 (5.52), 535 (4.41), 556 (4.55), 570 nm (4.53); MS (MALDI-TOF): $m/z = 1126.99$ [M^++2−C_2H_4]; HRMS (FAB$^+$): calcd for $C_{70}H_{78}N_8NiZn+H^+$: 1155.5027; found: 1155.5028.

Retro-Diels–Alder reaction conditions: A sample tube containing the appropriate bicyclo[2.2.2]octadiene-fused porphyrin dimer was placed in a flask, and the flask was evacuated by means of a rotary vacuum pump. The flask was then placed in a pre-heated glass tube oven at 200 °C. The red color of the porphyrin dimer immediately turned to black. After 1 h, the flask was cooled and then flushed with argon. The fully conjugated oligomers were obtained in quantitative yields and were sufficiently pure for our purposes.

Dimer 13–Zn$_2$: Green powder; m.p. > 250 °C; ^{1}H NMR (C_5D_5N): $\delta = 1.19$ (t, $J = 7.3$ Hz, 12H), 1.85 (m, 8H), 1.96 (t, $J = 7.3$ Hz, 12H), 2.37 (m, 8H), 3.97 (s, 12H), 4.12–4.22 (m, 16H), 10.15 (s, 4H), 10.99 (s, 4H), 11.48 ppm (s, 2H); ^{13}C NMR (C_5D_5N): $\delta = 12.1$, 14.5, 19.1, 20.4, 23.5, 26.9, 36.1, 95.7, 99.0, 114.4, 136.1, 140.5, 142.3, 142.5, 147.4, 147.5, 148.1, 150.7 ppm; UV/Vis (1% C_5H_5N/$CHCl_3$): λ_{max} ($\log\varepsilon$) = 333 (4.72), 390 (4.98), 412 (4.91), 444 (4.90), 474 (5.40), 525 (4.20), 579 (4.41), 621 (4.78), 636 nm (5.27); MS (MALDI-TOF): $m/z = 1162.93$ [M^++4]; elemental analysis calcd (%) for $C_{70}H_{78}N_8Zn_2$: C 72.34, H 6.76, N 9.64; found: C 72.08, H 6.89, N 9.36.

Dimer 13-H$_2$: Green powder; m.p. > 250 °C; ^{1}H NMR ($CDCl_3$/TFA): $\delta = -2.25$ (very broad signal), 1.10 (t, $J = 7.3$ Hz, 12H), 1.63–1.73 (m, 8H), 1.76 (t, $J = 7.3$ Hz, 12H), 2.10–2.20 (m, 8H), 3.88 (s, 12H), 4.10–4.22 (m, 16H), 10.64 (s, 4H), 11.45 (s, 4H), 11.81 ppm (s, 2H); ^{13}C NMR ($CDCl_3$/TFA): $\delta = 12.0$, 13.8, 17.4, 20.0, 23.0, 26.6, 34.3, 95.1, 100.5, 119.7, 134.7, 136.9, 137.1, 140.1, 140.6, 140.9, 143.4, 144.3 ppm; UV/Vis (1% TFA/$CHCl_3$): λ_{max} ($\log\varepsilon$) = 384 (5.26), 484 (4.49), 541 (4.42), 570 (4.45), 598 (4.55), 656 nm (5.23); MS (MALDI-TOF): $m/z = 1035.97$ [M^++1]; elemental analysis calcd (%) for $C_{70}H_{82}N_8 \cdot 1/2\,H_2O$: C 80.50, H 8.01, N 10.73; found: C 80.36, H 7.88, N 10.53.

Dimer 13–NiZn: Green powder; m.p. > 250 °C; ^{1}H NMR (C_5D_5N): $\delta = 1.17$ (t, $J = 7.3$ Hz, 6H), 1.23 (brs, 6H), 1.88 (m, 4H), 2.03 (t, $J = 7.3$ Hz, 6H), 2.17 (brs, 4H), 2.47 (m, 4H), 2.62 (brs, 6H), 3.14 (brs, 4H), 3.50 (brs, 2H), 3.80 (s, 6H), 4.23 (q, $J = 7.6$ Hz, 4H), 4.32 (t, $J = 7.6$ Hz, 4H), 5.69 (brs, 6H), 8.70 (brs, 4H), 9.14 (brs, 4H), 10.60 (s, 2H), 12.07 (brs, 2H), 15.30 ppm (brs, 2H); a signal due to two *meso* protons of the nickel–porphyrin unit was not identified; UV/Vis (pyridine): λ_{max} ($\log\varepsilon$) = 389 (4.94), 470 (5.13), 477 (5.15), 579 (4.41), 619 (4.73), 635 nm (5.21).

Dimer 17: Green powder; m.p. > 250 °C; ^{1}H NMR (C_5D_5N): $\delta = 1.23$ (brs, 6H), 2.07 (m, 18H), 2.17 (brs, 4H), 2.63 (brs, 6H), 3.13 (brs, 4H), 3.58 (brs, 2H), 4.22 (q, $J = 7.3$ Hz, 4H), 4.30 (m, 8H), 5.60 (brs, 6H), 8.70 (brs, 4H), 9.14 (brs, 4H), 10.60 (s, 2H), 12.14 (brs, 2H), 15.40 ppm (brs, 2H); a signal due to two *meso* protons of the nickel–porphyrin unit was not identified; UV/Vis (pyridine): λ_{max} ($\log\varepsilon$) = 390 (4.82), 469 (5.02), 477 (5.04), 579 (4.30), 620 (4.63), 634 nm (5.10).

X-ray analysis: The selected single crystal was mounted in a Lindemann glass capillary with a tiny amount of the mother liquor. X-ray measurements were carried out on either a Rigaku AFC7S with a Cu target (room temperature) or a Rigaku Mercury-7 with an Mo target (low temperatures). The diffraction data were processed with CrystalStructure, solved with SIR-97 or DIRDIF-99, and refined with SHELX-97. In the event of the solvent molecules not being adequately modeled, the core porphyrin molecules were refined without the solvent molecules by a combination of the SHELX-97 and PLATON SQUEEZE programs. CCDC-284573–284577 [**16**·1.5 PhCl(CCM), **16**·1.5 PhCl(CCI), **16**·6 $CHCl_3$, and **13**·4 C_5H_5N] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif/.

Acknowledgements

This work was partially supported by a Grand-in-Aid for Scientific Research B (17350022) from the Ministry of Education, Culture, Science, Sports and Technology, Japan. We appreciate the Research Center for Molecular-Scale Nanoscience, of the Institute for Molecular Science, for permitting us to carry out X-ray measurements (AFC7R-Mercury CCD).

[1] a) M. Berliocchi, M. Manenti, A. Bolognesi, A. Di Carlo, P. Ligli, R. Paolesse, F. Mandoy, C. Di Natale, E. Proiette, G. Petrocco, A. D'Amico, *Semicond. Sci. Technol.* **2004**, *19*, S354–S356; b) C. D. Dimitrakopoulos, D. J. Mascaro, *IBM J. Res. Dev.* **2001**, *45*, 11–30; c) N. R. Armstrong, *J. Porphyrins and Phthalocyanines* **2000**, *4*, 414–417; d) P. Alivisatos, P. F. Barbara, A. W. Castleman, J. Chang, D. A. Dixon, M. L. Klein, G. L. McLendon, J. S. Miller, M. A. Ratner, P. J. Rossky, S. I. Stupp, M. E. Thompson, *Adv. Mater.* **1998**, *10*, 1297–1336, and references therein.

[2] a) P. Thordarson, A. Marquis, M. J. Crossley, *Org. Biomol. Chem.* **2003**, *1*, 1216–1225; b) M. J. Crossley, P. Thordarson, *Angew. Chem.* **2002**, *114*, 1785–1788; *Angew. Chem. Int. Ed.* **2002**, *41*, 1709–1712; M. J. Crossley, L. A. Johnston, *Chem. Commun.* **2002**, 1122–1123; c) R. Beavington, P. L. Burn, *J. Chem. Soc. Perkin Trans. 1* **2000**, 1231–1240; d) R. Beavington, P. L. Burn, *J. Chem. Soc. Perkin Trans. 1* **2000**, 605–609; e) J. R. Reimers, T. X. Lu, M. J. Crossley, N. S. Hush, *Chem. Phys. Lett.* **1996**, *256*, 353–359; f) M. J. Crossley, P. L. Burn, *J. Chem. Soc. Chem. Commun.* **1987**, 39–40.

[3] a) R. Paolesse, L. Jaquinod, F. Della Sala, D. J. Nurco, L. Prodi, M. Montalti, C. Di Natale, A. D'Amico, A. Di Carlo, P. Lugli, K. M. Smith, *J. Am. Chem. Soc.* **2000**, *122*, 11295–11302; b) L. Jaquinod, O. Siri, R. G. Khoury, K. M. Smith, *Chem. Commun.* **1998**, 1261–1262; c) N. Kobayashi, M. Numao, R. Kondo, S. Nakajima, T. Osa, *Inorg. Chem.* **1991**, *30*, 2241–2244.

[4] M. G. H. Vicente, M. T. Cancilla, C. B. Lebrilla, K. M. Smith, *Chem. Commun.* **1998**, 2355–2356.

[5] a) A. Tsuda, A. Osuka, *Science* **2001**, *293*, 79–82; b) A. Tsuda, H. Furuta, A. Osuka, *J. Am. Chem. Soc.* **2001**, *123*, 10304–10321; c) N. Aratani, A. Tsuda, A. Osuka, *Synlett* **2001**, 1663–1674; d) A. Tsuda, A. Nakano, H. Furuta, H. Yanomochi, A. Osuka, *Angew. Chem.* **2000**, *112*, 572–575; *Angew. Chem. Int. Ed.* **2000**, *39*, 558–561; e) K. Sugiura, T. Matsumoto, S. Ohkouchi, Y. Naitoh, T. Kawai, Y. Takai, K. Ushiroda, K. Sakata, *Chem. Commun.* **1999**, 1957–1958.

[6] a) T. Okujima, N. Komobuchi, Y. Shimizu, H. Uno, N. Ono, *Tetrahedron Lett.* **2004**, *45*, 5461–5464; b) N. Ono, K. Kuroki, E. Watanabe, N. Ochi, H. Uno, *Heterocycles* **2004**, *62*, 365–373; c) H. Uno, T. Ishikawa, T. Hoshi, N. Ono, *Tetrahedron Lett.* **2003**, *44*, 5163–5165, and references therein.

[7] S. Ito, K. Nakamoto, H. Uno, T. Murashima, N. Ono, *Chem. Commun.* **2001**, 2696–2697.

[8] H. Uno, A. Masumoto, N. Ono, *J. Am. Chem. Soc.* **2003**, *125*, 12082–12083.
[9] a) H. Uno, S. Ito, M. Wada, H. Watanabe, M. Nagai, A. Hayashi, T. Murashima, N. Ono, *J. Chem. Soc. Perkin Trans. 1* **2000**, 4347–4355; b) Y. Abel, F.-P. Montforts, *Tetrahedron Lett.* **1997**, *38*, 1745–1748.
[10] a) A. Boudif, M. Momenteau, *J. Chem. Soc. Chem. Commun.* **1994**, 2069–2070; b) A. Boudif, M. Momenteau, *J. Chem. Soc. Perkin Trans. 1* **1996**, 1235–1242; c) J. L. Sessler, J. W. Genge, A. Urbach, P. Sanson, *Synlett* **1996**, 187–188; d) T. D. Lash, P. Chandrasekar, A. T. Osuma, S. T. Chaney, J. D. Spence, *J. Org. Chem.* **1998**, *63*, 8455–8469.
[11] K. M. Smith, in *The Porphyrin Handbook, Vol. 1* (Eds.: M. K. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, **1999**, p. 2–44.
[12] a) J. L. Sessler, M. R. Johnson, V. Lynch, *J. Org. Chem.* **1987**, *52*, 4394–4397; b) S. V. Shevchuk, J. M. Davis, J. L. Sessler, *Tetrahedron Lett.* **2001**, *42*, 2447–2450.
[13] J. L. Sessler, A. Mozaffari, M. R. Martin, *Org. Synth.* **1998**, *9*, 242–249.
[14] J. B. Paine III, D. Dolphin, M. Gouterman, *Can. J. Chem.* **1978**, *56*, 1712–1714.
[15] "Photochemistry of Porphyrins and Metalloporphyrins": F. R. Hopf, D. G. Whitten, in *Porphyrins and Metalloporphyrins* (Ed.: K. M. Smith), Elsevier, Amsterdam, **1975**, Chapter 16.
[16] a) SHELXL-97, program for refinement of crystal structures from diffraction data, University of Göttingen, Göttingen (Germany); G. Scheldrick, T. Schneider, *Methods Enzymol.* **1997**, *277*, 319–343; b) PLATON, a multipurpose crystallographic tool, Utrecht Univesity, Utrecht (The Netherlands); A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7–13.
[17] J. A. Shelnutt, in *The Porphyrin Handbook, Vol. 7* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, **2000**, p. 167–224.
[18] G. D. Hatmen, L. M. Weinstock, *Org. Synth.* **1988**, *6*, 620–628.
[19] S. Ito, N. Ochi, T. Murashima, H. Uno, N. Ono, *Heterocycles* **2000**, *52*, 399–411.

Received: November 16, 2006
Published online: March 30, 2007

