CHEMISTRY
A EUROPEAN JOURNAL

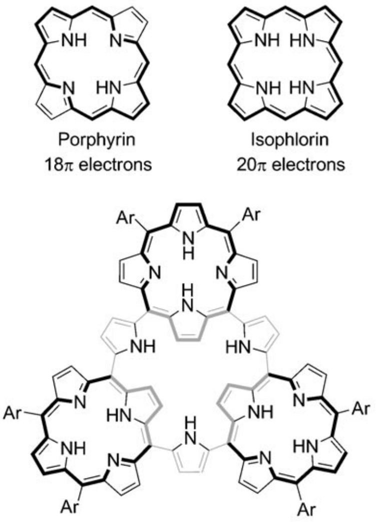
DOI: 10.1002/chem.201002219

Pyrrole-Bridged Porphyrin Nanorings

Jianxin Song,[a] Naoki Aratani,*[a, b] Hiroshi Shinokubo,*[c] and Atsuhiro Osuka*[a]

Covalently linked, cyclic porphyrin arrays have been explored mainly as artificial photosynthetic antennae and large host molecules.[1–3] In such arrays, a variety of bridges that connect porphyrins have been employed to control the overall molecular shape and to tune the electronic interaction between neighboring porphyrins. Among these, acetylenic spacers have been often used, because these are easy to incorporate into porphyrin arrays and allow for elongation of conjugation networks.[3] As a different approach, we have explored various cyclic porphyrin arrays by direct *meso–meso* coupling reactions on the basis of Ag^I-promoted coupling and Suzuki–Miyaura coupling.[1e,4] In recent years, we have also explored aromatic heterocycle-bridged cyclic porphyrin arrays. The β-to-β 2,6-pyridylene-bridged cyclic porphyrin arrays exhibit relatively large fluorescence quantum yields and long fluorescent lifetimes,[5] and β-to-β 2,5-thienylene-bridged cyclic porphyrin arrays exhibit large two-photon absorption (TPA) cross-section values, owing to effective electronic delocalization through the thienylene linkages.[6] Zinc(II) complexes of *meso*-to-*meso* 2,2′-bithiophene-bridged cyclic porphyrin arrays are suitable for multicharge storage and hence are of interest as molecular information storage systems.[7]

As an extension of these studies, we attempted to synthesize *meso*-to-*meso* 2,5-pyrrolylene-bridged cyclic porphyrin arrays. A pyrrole bridge in cyclic porphyrin nanorings is quite attractive in view of its electron-rich properties, effective conjugation, and possible hydrogen-bonding donating ability. In addition, as indicated for the cyclic porphyrin trimer in Scheme 1, we can consider a formal hexaphyrin-like π-electronic network[8] that is spread across the pyrrole bridges and the parts of porphyrin skeleton. Therefore, *meso*-to-*meso* pyrrolylene-bridged cyclic porphyrin arrays are expected to lead to new porphyrinic molecules with intriguing electronic properties. However, manipulation of pyrroles is not trivial, because of their instability and high reactivity. As a consequence, there are only scattered examples of pyrrole-appended porphyrins in the literature.[9] Quite recently, we have reported Cu^I-mediated annulation of 1,3-butadiyne-bridged diporphyrin with various amines to provide 2,5-pyrrolylene-bridged diporphyrins in moderate to good yields.[10] In these diporphyrins, notable electronic in-



Scheme 1. Porphyrin, isophlorin, and a hybrid porphyrinoid.

---

[a] Dr. J. Song, Dr. N. Aratani, Prof. Dr. A. Osuka
Department of Chemistry
Graduate School of Science, Kyoto University
Sakyo-ku, Kyoto 606-8502 (Japan)
Fax: (+81)75-753-3970
E-mail: aratani@kuchem.kyoto-u.ac.jp
osuka@kuchem.kyoto-u.ac.jp

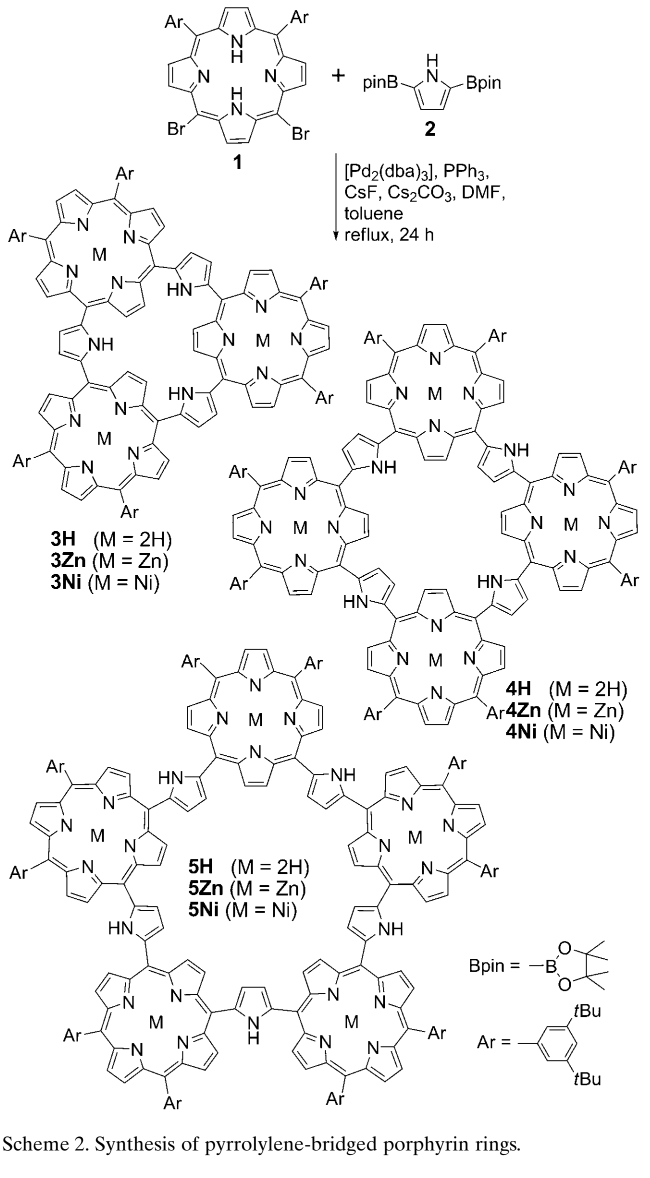
[b] Dr. N. Aratani
PRESTO Japan Science and Technology Agency (Japan)

[c] Prof. Dr. H. Shinokubo
Department of Applied Chemistry
Graduate School of Engineering
Nagoya University, Chikusa-ku, Nagoya 464-8603 (Japan)
Fax: (+81)52-789-5113
E-mail: hshino@apchem.nagoya-u.ac.jp

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201002219.

teractions were observed in the absorption and fluorescence spectra, which vary upon the pyrrolic *N*-substituent.

Here we wish to report the efficient synthesis of *meso*-to-*meso* 2,5-pyrrolylene-bridged porphyrin nanorings **3**–**5** from porphyrin **1** and pyrrole **2** through Suzuki–Miyaura coupling (Scheme 2). Interestingly, resonance contributors of these nanorings can be regarded as ([18]annuleno)$_3$[30]annulene, ([18]annuleno)$_4$[40]annulene, and ([18]annuleno)$_5$[50]annulene for **3**–**5**, respectively. Annulenoannulenes that consist of multi-annulated aromatic annulenes have been extensively investigated in terms of their possible overall aromaticity.[11] In these three cases, the central resonance contributors (shown in gray in Scheme 1) correspond to so-called expanded isophlorins. Isophlorin (*N*,*N*′-dihydroporphyrin) is a reduced 20π-electron congener of porphyrin, in which the macrocyclic conjugation surrounds the carbon periphery. In recent years, the chemistry of isophlorins has been reactivated in light of its relevance to antiaromatic porphyrins.[12–14]



Scheme 2. Synthesis of pyrrolylene-bridged porphyrin rings.

Synthesis of pyrrole-bridged porphyrin rings **3H**–**5H** is straightforward through Suzuki–Miyaura cross-coupling of 5,10-diaryl-15,20-dibromoporphyrin **1**[2d] and 2,5-diborylpyrrole **2**[15] (Scheme 2). Separation by gel-permeation chromatography (GPC) and silica-gel chromatography afforded pyrrole-bridged cyclic porphyrin 3-mer **3H** (13%), 4-mer **4H** (5.3%), and 5-mer **5H** (2.7%). Notably, the reaction represents a rare example of one-pot synthesis of such large cyclic arrays from a monomeric porphyrin precursor without template molecules.

Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra of the cyclic porphyrin arrays displayed the parent ion peaks at *m*/*z* 2250.2995 for **3H** (calcd for $C_{156}H_{166}N_{15}=2250.3413$ $[M+H]^+$), 2999.7303 for **4H** (calcd for $C_{208}H_{220}N_{20}=2999.7902$ $[M]^+$), and 3750.2339 for **5H** (calcd for $C_{260}H_{275}N_{25}=3750.2415$ $[M]^+$) (see also the Supporting Information). The ^{1}H NMR spectrum of **3H** in $CDCl_3$ was quite simple, exhibiting two singlet and two doublet peaks for the β-protons at 10.44, 9.85, 9.12, and 8.88 ppm, a singlet for the bridging-pyrrole NH protons at 10.62 ppm, a singlet for the inner NH protons at −2.25 ppm, and a doublet for the bridging-pyrrole β-protons at 8.00 ppm, while no *meso*-proton signal was observed. Interestingly two *ortho*-protons of aryl substituents were distinguished, because of restricted rotation of the pyrrole bridges at room temperature. The electronic system is potentially attractive in view of their structural analogy to that of ([18]annuleno)$_3$[30]annulene; however, the ^{1}H NMR exhibited no ring current arising from 30π circuit. This can be probably ascribed to strongly localized porphyrin π circuits. The twist between the planes of the bridging pyrroles and the porphyrins (specified later as 42–76°) might contribute towards the localization of the porphyrin π circuits. The ^{1}H NMR spectra of **4H** and **5H** displayed similar chemical shifts for **3H**, but the one doublet peak of *ortho*-protons was observed, indicating their more flexible conformations in solution that lead to the simple ^{1}H NMR spectra (Supporting Information). Consequently, the spectral data were in line with the highly symmetric cyclic structures of **3H**–**5H** in solution. Again, **4H** and **5H** hold the formal octaphyrin and decaphyrin structures in their cores, but exhibit no specific ring current effects.

Free-base cyclic arrays **3H**–**5H** were converted into the corresponding zinc(II) and nickel(II) complexes **3Zn**–**5Zn**, and **3Ni**–**5Ni** upon treatment with $Zn(OAc)_2$ and $Ni(OAc)_2$, respectively. Single crystals of **3Ni** suitable for X-ray diffraction analysis were grown by vapor slow diffusion of 2-propanol and methanol into a solution of **3Ni** in chlorobenzene (Figure 1).[16] The X-ray crystal analysis revealed a symmetric solid-state structure in which three of the pyrrole units point into the core. The pyrrole moieties are tilted by 42–76° relative to the porphyrin mean planes, which consist of four core nitrogen atoms. The total molecular conformation is a dome shape, and the center-to-center distances between the nickel ions are 10.8, 10.9, and 11.4 Å. The bond lengths

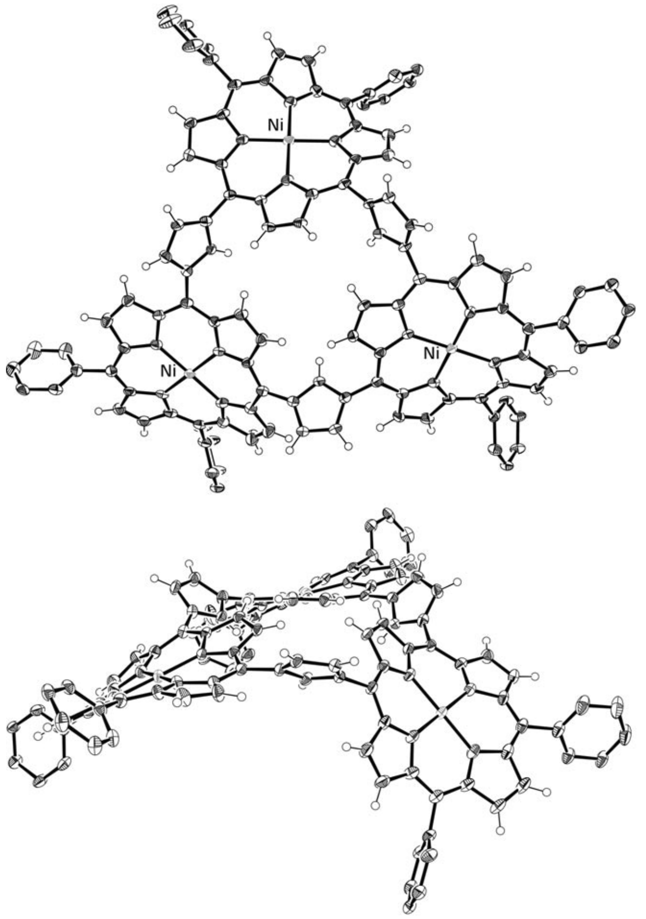


Figure 1. X-ray crystal structure of **3Ni**. Top view (top) and side view (bottom). The thermal ellipsoids are 50% probability level. Substituents on phenyl groups and solvent molecules are omitted for clarity.

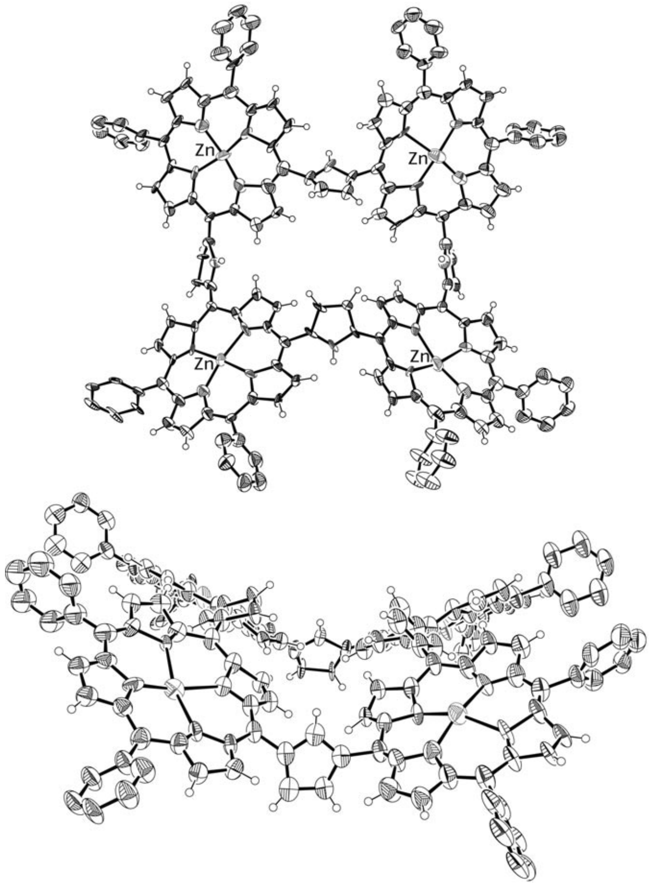


Figure 2. X-ray crystal structure of **4Zn**. Top view (top) and side view (bottom). The thermal ellipsoids are 50% probability level. Substituents on phenyl groups and solvent molecules are omitted for clarity.

between the porphyrin and the neighboring pyrrole (1.46–1.49 Å) are slightly shorter than normal C−C single bonds. This structure is consistent with the ^{1}H NMR spectral pattern.

Single crystals of **4Zn** were grown by vapor slow diffusion of ethanol into a solution of **4Zn** in toluene (Figure 2).[17] The X-ray crystal analysis revealed a nonsymmetric solid-state structure in which two opposite nitrogen atoms of the bridging pyrrole rings point into the core and the rest out of the core, thus maintaining the overall planarity of the system. The center-to-center distances between the zinc atoms are about 11.2 Å. The pyrrole moieties are tilted by 44–62° relative to the porphyrin mean planes.

The UV/Vis absorption spectra of **3Zn**–**5Zn** in CH_2Cl_2 are shown in Figure 3a. The UV/Vis absorption spectrum of **3Zn** shows a split Soret band at 416 and 456 nm and Q-bands at 559 and 632 nm. This split Soret bands of **3Zn** can be understood in terms of the exciton coupling theory owing to the close proximity of center-to-center distance ($\approx$11 Å).[18]

It is appropriate to place two perpendicular transition dipole moments of each porphyrin unit. The in-line component of transition dipoles leads to a red-shifted Soret band (456 nm), while the small absorption shoulder at 416 nm in **3Zn** may be considered in terms of H-type dipole–dipole coupling of parallel components. It is likely that the observed intensity of the split Soret bands reflects the relative amplitude of the strong interacting (in-line) component to the weak (parallel) one. The UV/Vis absorption spectra of **4Zn** and **5Zn** also exhibit split Soret bands, but their splitting extents are smaller than that of **3Zn**. The observed larger splitting energy of **3Zn** may reflect its more rigid conformation, while in **4Zn** and **5Zn**, the flexible conformations may lead to distribution of many conformers, which exhibit different exciton coupling. This situation leads to averaged and thus weaker exciton coupling. The absorption spectra of **3H**–**5H** are very similar to those of the corresponding Zn^{II} complexes (Figure 3b). The fluorescence spectra of **3Zn**–**5Zn** exhibit a broad structure (Figure 3c). The fluorescence quantum yields in CH_2Cl_2 at room temperature are 0.040, 0.067, and 0.076 for **3Zn**–**5Zn**, and 0.035, 0.065, and 0.070 for **3H**–**5H**, respectively. Interestingly both series indicate the increase in the fluorescence quantum yield upon the increase in size.

The electrochemical properties of **3Zn**–**5Zn** were investigated by cyclic voltammetry. Although the first oxidation potential waves of **3Zn**–**5Zn** could not be identified clearly,

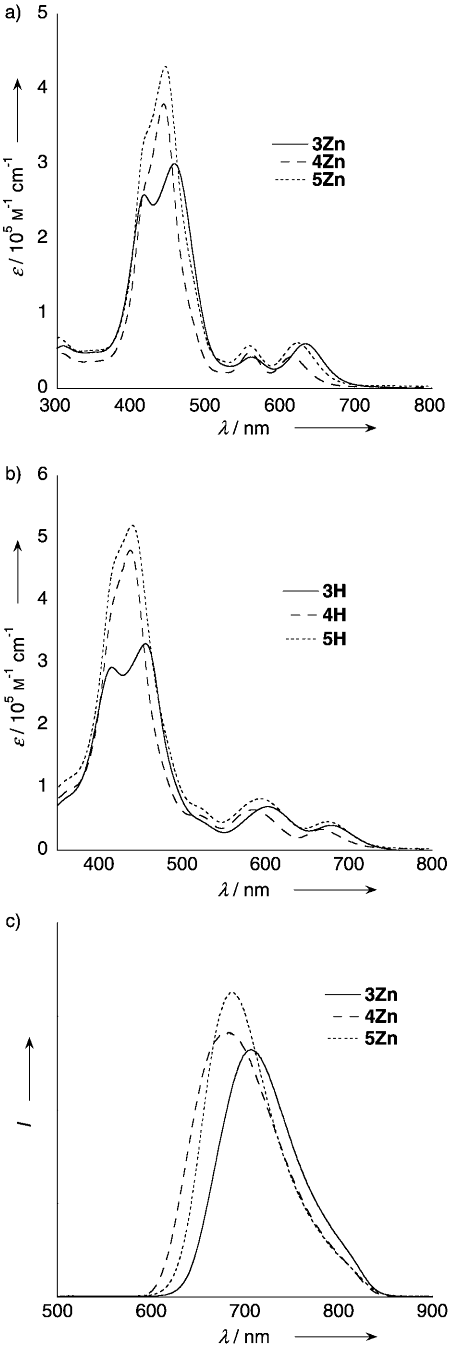


Figure 3. UV/Vis absorption spectra of a) **3Zn**–**5Zn**, and b) **3H**–**5H**, and c) fluorescence spectra of **3Zn**–**5Zn** in CH_2Cl_2.

they were split into several waves, indicating the substantial electronic interaction between the porphyrins through the pyrrole spacer (Supporting Information). Porphyrin **3Zn** underwent reversible oxidation at around 0.26 (quasi-two-electron process) and 0.36 V (one-electron process; versus Ag/Ag^+); these have been assigned as split first oxidation waves (one electron per porphyrin) judging from the results of other electronically coupled diporphyrins,[10] while poorly resolved reversible oxidation potentials around 0.3 V were detected in **4Zn** and **5Zn**. These features should arise from the influence of the positive charge of the first-generated Zn^{II}–porphyrin radical cations.

In conclusion, we prepared a 3-mer, 4-mer, and 5-mer series of *meso*-to-*meso* pyrrolylene-bridged cyclic porphyrins through one-pot Suzuki–Miyaura coupling reaction from dibromoporphyrin monomer. The ^1H NMR spectra of these cyclic compounds revealed their highly symmetric structures in solution, although the 1,3-alternative structure was observed in the solid state of **4Zn**. The UV/Vis absorption spectra of the **3Zn**–**5Zn** indicate the strong excitonic interactions between porphyrin units. Because the cyclic arrays have strong excitonic and electronic couplings between porphyrin units, the coherent and/or incoherent energy hopping processes are easily expected. Also, investigation on longer oligopyrrole bridged cyclic porphyrin arrays is currently in progress.

Acknowledgements

This work was partially supported by Grants-in-Aid for Scientific Research from MEXT, Japan (22245006 (A), 21685011, and 20108001 “pi-Space”) and the PRESTO program from JST, Japan. H.S. gratefully acknowledges financial support from the Toray Science Foundation. The authors thank Prof. H. Maeda, T. Hashimoto and Y. Haketa, Ritsumeikan University, for MALDI-TOF MS measurements.

Keywords: aromaticity · cross-coupling · exciton coupling · porphyrinoids · pi conjugation

---

[1] a) Y. Nakamura, N. Aratani, A. Osuka, *Chem. Soc. Rev.* **2007**, *36*, 831; b) J. R. Reimers, N. S. Hush, M. J. Crossley, *J. Porphyrins Phthalocyanines* **2002**, *6*, 795; c) K. Sugiura, *Top. Curr. Chem.* **2003**, *228*, 65; d) D. Kim, A. Osuka, *Acc. Chem. Res.* **2004**, *37*, 735; e) N. Aratani, D. Kim, A. Osuka, *Acc. Chem. Res.* **2009**, *42*, 1922.

[2] a) S. Anderson, H. L. Anderson, J. K. M. Sanders, *Acc. Chem. Res.* **1993**, *26*, 469; b) D. Holten, D. F. Bocian, J. S. Lindsey, *Acc. Chem. Res.* **2002**, *35*, 57; c) S. Rucareanu, A. Schuwey, A. Gossauer, *J. Am. Chem. Soc.* **2006**, *128*, 3396; d) A. Kato, K. Sugiura, H. Miyasaka, H. Tanaka, T. Kawai, M. Sugimoto, M. Yamashita, *Chem. Lett.* **2004**, *33*, 578.

[3] a) M. Hoffmann, C. J. Wilson, B. Odell, H. L. Anderson, *Angew. Chem.* **2007**, *119*, 3183; *Angew. Chem. Int. Ed.* **2007**, *46*, 3122; b) M. Hoffmann, J. Kärnbratt, M.-H. Chang, L. M. Herz, B. Albinsson, H. L. Anderson, *Angew. Chem.* **2008**, *120*, 5071; *Angew. Chem. Int. Ed.* **2008**, *47*, 4993.

[4] a) X. Peng, N. Aratani, A. Tsuda, A. Takagi, T. Matsumoto, T. Kawai, I.-W. Hwang, T. K. Ahn, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2004**, *126*, 4468; b) Y. Nakamura, I.-W. Hwang, N. Aratani, T. K. Ahn, D. M. Ko, A. Takagi, T. Kawai, T. Matsumoto, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2005**, *127*, 236; c) Y. Nakamura, N. Aratani, H. Shinokubo, A. Takagi, T. Kawai, T. Matsumoto, Z. S. Yoon, D. K. Kim, T. K. Ahn, D. Kim, A. Muranaka, N. Kobayashi, A. Osuka, *J. Am. Chem. Soc.* **2006**, *128*, 4119; d) T. Hori, N. Aratani, A. Takagi, T. Matsumoto, T. Kawai, M.-C. Yoon, Z. S. Yoon, D. Kim, A. Osuka, *Chem. Eur. J.* **2006**, *12*, 1319; e) N. Aratani, A. Osuka, *Chem. Commun.* **2008**, 4067.

[5] J. Song, P. Kim, N. Aratani, D. Kim, H. Shinokubo, A. Osuka, *Chem. Eur. J.* **2010**, *16*, 3009.

[6] J. Song, S. Y. Jang, S. Yamaguchi, J. Sankar, S. Hiroto, N. Aratani, J.-Y. Shin, S. Easwaramoorthi, K. S. Kim, D. Kim, H. Shinokubo, A.

Osuka, *Angew. Chem.* **2008**, *120*, 6093; *Angew. Chem. Int. Ed.* **2008**, *47*, 6004.

[7] K. Osawa, J. Song, K. Furukawa, H. Shinokubo, N. Aratani, A. Osuka, *Chem. Asian J.* **2010**, *5*, 764.

[8] For chemistry of expanded porphyrins, see: a) A. Jasat, D. Dolphin, *Chem. Rev.* **1997**, *97*, 2267; b) H. Furuta, H. Maeda, A. Osuka, *Chem. Commun.* **2002**, 1795; c) J. L. Sessler, D. Seidel, *Angew. Chem.* **2003**, *115*, 5292; *Angew. Chem. Int. Ed.* **2003**, *42*, 5134; d) T. K. Chandrashekar, S. Venkatraman, *Acc. Chem. Res.* **2003**, *36*, 676; e) S. Shimizu, A. Osuka, *Eur. J. Inorg. Chem.* **2006**, 1319; f) J. M. Lim, Z. S. Yoon, J.-Y. Shin, K. S. Kim, M.-C. Yoon, D. Kim, *Chem. Commun.* **2009**, 261.

[9] a) P. S. Clezy, A. J. Liepa, N. W. Webb, *Aust. J. Chem.* **1972**, *25*, 1991; b) H. Aota, Y. Itai, A. Matsumoto, M. Kamachi, *Chem. Lett.* **1994**, 2043; c) D. Yashunsky, G. V. Ponomarev, D. P. Arnold, *Tetrahedron Lett.* **1997**, *38*, 105; d) H. Furuta, H. Maeda, T. Furuta, A. Osuka, *Org. Lett.* **2000**, *2*, 187; e) A. M. G. Silva, A. C. Tomé, M. G. P. M. S. Neves, A. M. S. Silva, J. A. S. Cavaleiro, *J. Org. Chem.* **2002**, *67*, 726; f) I. Schmidt, J. Jiao, P. Thamyongkit, D. S. Sharada, D. F. Bocian, J. S. Lindsey, *J. Org. Chem.* **2006**, *71*, 3033; g) I. Saltsman, I. Goldberg, Y. Balasz, Z. Gross, *Tetrahedron Lett.* **2007**, *48*, 239.

[10] C. Maeda, H. Shinokubo, A. Osuka, *Org. Lett.* **2010**, *12*, 1820.

[11] a) E. Vogel, H.-V. Runzheimer, F. Hogrefe, B. Baasner, J. Lex, *Angew. Chem.* **1977**, *89*, 909; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 871; b) K. Müllen, J. F. M. Oth, H.-W. Engels, E. Vogel, *Angew. Chem.* **1979**, *91*, 251; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 229; c) M. Nakagawa, *Angew. Chem.* **1979**, *91*, 215; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 202; d) M. Oda, *Pure Appl. Chem.* **1986**, *58*, 7.

[12] a) J. A. Cissell, T. P. Vaid, A. L. Rheingold, *J. Am. Chem. Soc.* **2005**, *127*, 12212; b) C. Liu, D.-M. Shen, Q.-Y. Chen, *J. Am. Chem. Soc.* **2007**, *129*, 5814; c) J. A. Cissell, T. P. Vaid, G. P. A. Yap, *J. Am. Chem. Soc.* **2007**, *129*, 7841; d) A. Weiss, M. C. Hodgson, P. D. W. Boyd, W. Siebert, P. J. Brothers, *Chem. Eur. J.* **2007**, *13*, 5982; e) Y. Matano, M. Nakashima, T. Nakabuchi, H. Imahori, S. Fujishige, H. Nakano, *Org. Lett.* **2008**, *10*, 553.

[13] Y. Yamamoto, A. Yamamoto, S. Furuta, M. Horie, M. Kodama, W. Sato, K. Akiba, S. Tsuzuki, T. Uchimaru, D. Hashizume, F. Iwasaki, *J. Am. Chem. Soc.* **2005**, *127*, 14540.

[14] T. Miura, T. Higashino, S. Saito, A. Osuka, *Chem. Eur. J.* **2010**, *16*, 55.

[15] J. Takagi, K. Sato, J. F. Hartwig, T. Ishiyama, N. Miyaura, *Tetrahedron Lett.* **2002**, *43*, 5649.

[16] Crystallographic data for **3Ni**: $C_{156}H_{159}N_{15}Ni_3\cdot(\mathrm{PhCl})_{2.485}\cdot(i\mathrm{PrOH})_{3.685}\cdot(\mathrm{MeOH})_{0.358}$, $M_r=2907.98$, triclinic, space group $P\bar{1}$ (no. 2), $a=18.401(3)$, $b=19.428(3)$, $c=25.183(4)$ Å, $\alpha=105.026(3)$, $\beta=106.858(3)$, $\gamma=90.738(3)°$, $V=8283(2)$ Å^3, $T=90(2)$ K, $Z=2$, reflections measured 42641, 28619 unique. The final R_1 was 0.0807 [$I>2\sigma(I)$], and the final wR on F^2 was 0.2516 (all data), GOF = 1.026. CCDC-779923 contains 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.

[17] Crystallographic data for **4Zn**: $C_{208}H_{212}N_{20}O_4Zn_4$, $M_r=3317.46$, monoclinic, space group Cc (no. 9), $a=61.414(18)$, $b=8.454(3)$, $c=49.699(15)$ Å, $\beta=114.579(4)°$, $V=23464(12)$ Å^3, $T=90(2)$ K, $Z=4$, reflections measured 46676, 26113 unique. The final R_1 was 0.1301 [$I>2\sigma(I)$], and the final wR on F^2 was 0.3384 (all data), GOF = 1.092. CCDC-779924 contains 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. The contributions to the scattering arising from the presence of the disordered solvents in the crystals of **4Zn** were removed by use of the utility SQUEEZE in the PLATON software package.[19]

[18] M. Kasha, H. R. Rawls, M. A. El-Bayoumi, *Pure Appl. Chem.* **1965**, *11*, 371.

[19] PLATON, A Multipurpose Crystallographic Tool, Squeeze-Platon, A. L. Spek, Utrecht, **2005**; P. van der Sluis, A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, 194.

Received: August 3, 2010