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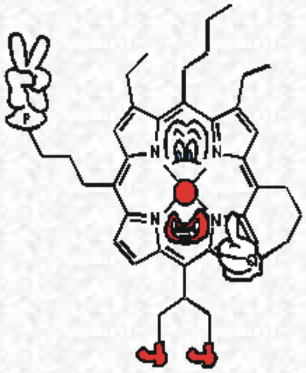
[C0029]

Conformationally Designed Biomimetic Macrocycles - Synthesis of Porphyrins and Porphodimethenes with Mixed Substitution Pattern and Distortion Modes



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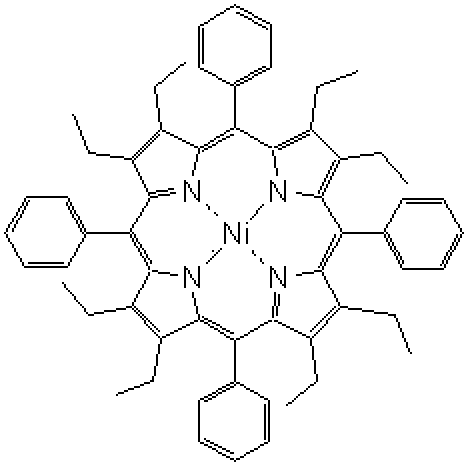
Introduction

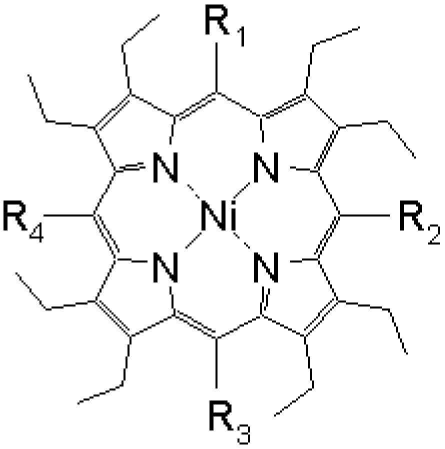
Conformationally designed biomimetic systems and the investigation of the conformation control of biological reactions is becoming a topic of active research at the interface of chemistry and biology.[1] In this context the interrelationship between macrocycle conformation and physicochemical properties in porphyrins is emerging as a topic of special biological relevance. Various nonplanar conformations have been observed for the porphyrinoid cofactors involved in photosynthesis, electron transfer and respiration and it is now believed that the physicochemical properties of the natural tetrapyrroles are fine-tuned via steric interactions with the protein skeleton in a conformational control process.[1b,c,2] For example, there is considerable structural heterogeneity in the accessory bacteriochlorophylls of photosynthesis[3] and a conformational asymmetry is one possible explanation for the unidirectonality of the light-induced electron transfer in the photosynthetic reaction center.[4] Similarly different cofactor conformations have been observed for and implied in the action of various heme proteins such as respiratory proteins,[5a] cytochromes,[5b] cytochrome P450[5c] and catalases.[5d] Indeed, dynamic conformation changes and redox dependent changes of the porphyrin conformation in proteins have now been established.[6] Different macrocycle conformations have also been described for diverse tetrapyrrole classes like corrins in B12 and F430[7a] and hydroporphyrins[7b] in sulfite and nitrite reductase[7c].[8]

In order to gain a better insight into these processes and to firmly establish conformational control as one process for the regulation of



(1)

the macrocycle properties a multitude of synthetic model compounds have been studied. [2] Nonplanar aromatic systems are accessible by synthesis of sterically strained systems and thus highly substituted porphyrins have been used prominently in this area.[2,9] So far most studies have been concerned with simple symmetric porphyrins.[2] Important examples, are 2,3,7,8,12,13,17,18-octaalkyl-5,10,15,20-tetraarylporphyrins (e.g. **1**), [10] 2,3,5,7,8,10,12,13,15,17,18,20-dodecarylporphyrins,[11] 2,3,5,7,8,10,12,13,15,-17,18,20-dodeca-alkylporphyrins,[10b,11b,12,13] 2,3,7,8,12,13,17,18-octahalogeno-5,10,15,20-tetraarylporphyrins, [10c,14] and 5,10,15,20-tetraalkylporphyrins.[15] Such porphyrins are easily accessible by condensation of 3,4-disubstituted pyrrole with the appropriate aldehyde or via halogenation of 5,10,15,20-tetraphenylporphyrin.[16]



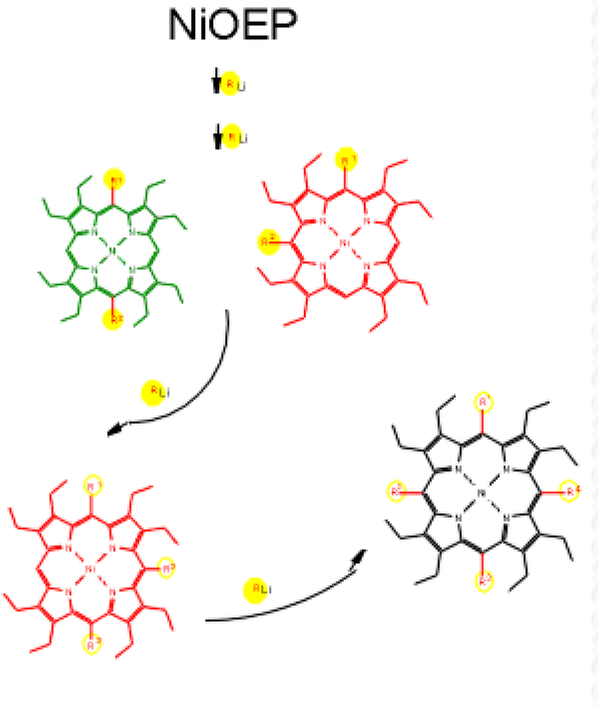
(2)

While for b substituent mixing synthetic strategies are in principle available a rational synthesis of porphyrins with different regiochemical arrangement of meso substituents was not possible until recently. Existing methods utilized either only theoretically possible multi-step total syntheses or mixed condensations of pyrroles and aldehydes requiring an inordinate laborious chromatographic work-up.[16] This lack of synthetic methodology has now been overcome with our development of the use of organolithium reagents for the meso functionalization of tetrapyrroles. [13a,17] The reaction of porphyrins with LiR proceeded via an addition-oxidation mechanism and allowed the meso substitution of porphyrins in excellent yields. Here we report that this reaction can be utilized for the synthesis of conformationally designed porphyrins with different type and number of meso substituents (**2**) with defined regiochemical arrangement and describe structural studies aimed at elucidating the conformational behavior of porphyrins with mixed distortion modes. An overview of the synthetic strategy is given in Scheme 1.

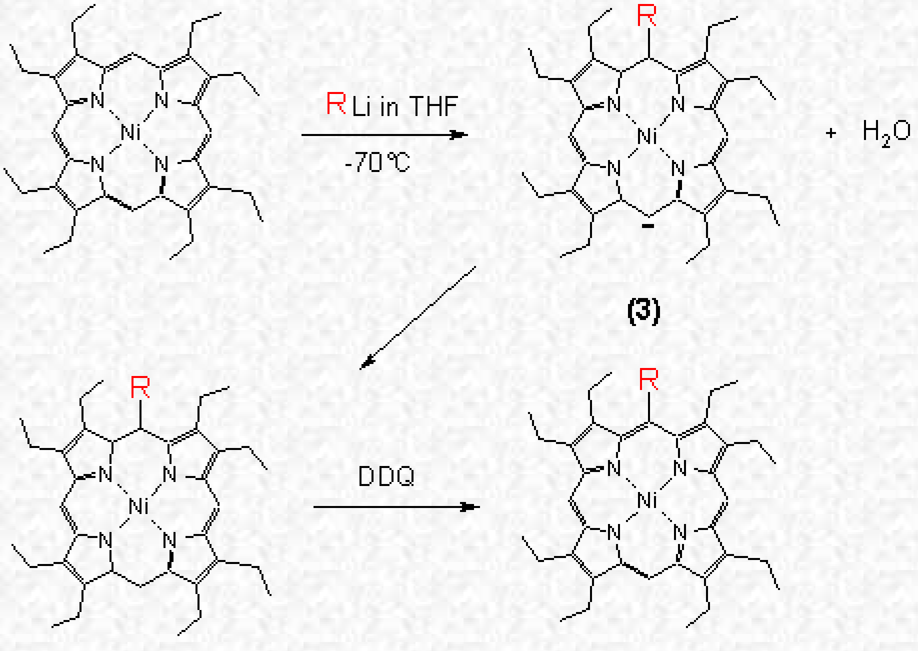
To investigate the correlation between the conformation of the macrocycles and its physicochemical properties, porphyrins with mixed meso substituent types are of special interest. The structures of S_4 symmetric dodecasubstituted, nonplanar porphyrins are well known. Meso alkyl groups lead to a ruffled distortion mode and aryl groups induce a saddle type conformation. As natural tetrapyrrole systems exhibit asymmetric substituent pattern the question arose to what extent a mixing of distortion modes can be achieved by rational variation of the meso-substituent pattern. We planned to synthesize porphyrins with different types and numbers of both meso alkyl and aryl substituents to investigate this problem.

Regioselective Synthesis of meso Substituted Porphyrins

The initial studies had shown that all meso positions can be substituted with LiR using four successive addition-oxidation cycles.[13a,18] Thus it should be possible to synthesize regiochemically pure porphyrins with different type and number of meso substituents by choosing the appropriate sequence for the individual LiR reagents. As described above, meso alkyl and meso aryl substituents flanked by b alkyl or aryl residues give rise to different distortion modes. Thus we chose BuLi and PhLi as standard reagents to test the feasibility of this approach. Octaethyl-porphyrin and its metal complexes were used as educts as a large body of structural data is available for highly substituted porphyrins that incorporate the octaethylporphyrin (**7**) motif.[2] For ease of NMR spectroscopic detection and as many comparative structural data are available for nickel(II) complexes most of the test reactions were performed using (2,3,7,8,12,13,17,18-octaethylporphyrinato)nickel(II) (**3**) as starting compound.

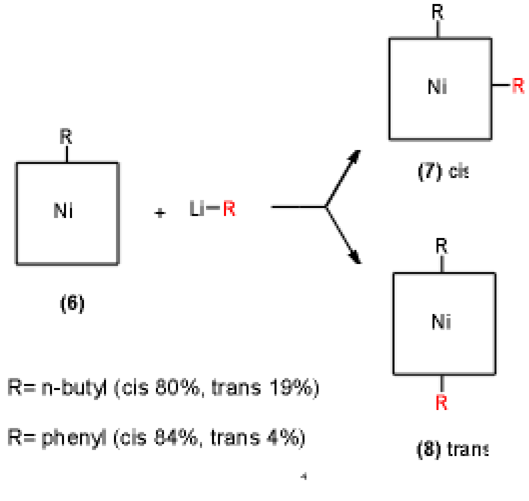


Scheme 1: General reaction scheme.



Scheme 2: Outline of the reaction mechanism.

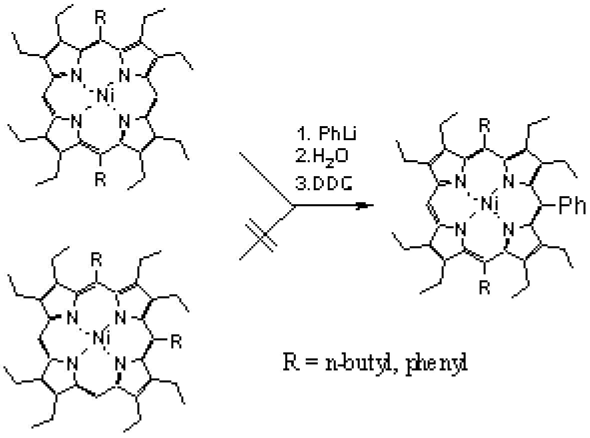
Formally, the reaction mechanism constitutes a nucleophilic substitution at the meso position of the porphyrin (Scheme 2). The addition of LiR leads to the formation of an anion (**4**). Hydrolysis yields a porphodimethene (**5**), which could be oxidized in most cases to the corresponding porphyrin (**5**, see below).



Scheme 3: Regiochemical aspects of the reaction.

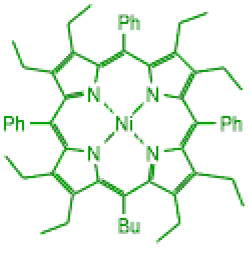
First, we studied the regioselectivity of the addition of a second meso substituent. Reac-tion of Ni(II)(2,3,7,8,-12,13,17,18-octaethyl-5-phenylporphyrinato) (**6**) with PhLi afforded the Ni-complex of *cis*-5,10-diphenylporphyrin (**7**) in 84 % and *trans*-5,15-diphenylporphyrin (**8**) in 4 % yield. As expected, phenyl lithium shows a higher selectivity com-pared to *n*-butyl lithium. A similar reaction of Ni(II)(5-butyl-2,3,7,8,12,-13,17,18-octaethylporphy-rinato) with *n*-butyl lithium gave the *cis*-product (**8**) in 80% and the *trans*-product (**7**) in 4% yield (Scheme 3).

One surprising result form these studies concerned the different reactivity of BuLi *versus* PhLi with 5,10-di- or 5,10,15-trisubstituted porphyrins. Generally, it was not possible to insert an aryl substituent in the 15 position of the (2,3,7,8,12,13,17,18-octaethylporphyrinato)nickel(II) skeleton that already contained substituents at the 5 and 10 position (Scheme 4).

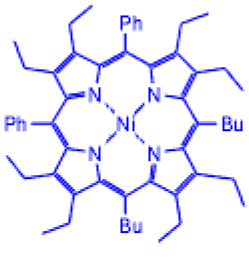


Scheme 4:

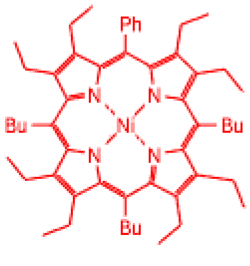
With this new method mixed aryl and alkyl substituents could be introduced in various regio chemical combinations and high yields by use of the respective organolithium reagents. For example, by repetition of the sequence shown in Scheme 1 with different residues (R = n-butyl or phenyl), four dodecasubstituted porphyrins (9, 10, 11, 12) with mixed substitution pattern were successfully prepared, indicating the synthetic utility of this reaction.



(9)



(10)



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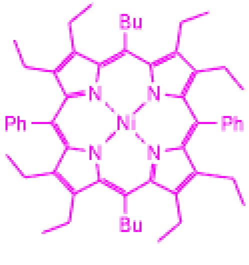


(12)

Preliminary crystal structure analyses indicate that the presence of both meso alkyl and aryl groups leads to macrocycles exhibiting ruffle and saddle distortion. The relative contribution of the individual distortion modes to the overall conformation depends on the type, number, and localization of the substituents. In line with expectations the absorption bands are shifted bathochromically with increasing number of meso substitutuents.

As one example the structure of an undecasubstituted nickel(II) porphyrin is shown in Figure 1. The structure exhibits an overall saddle distortion with significant displacements of the alkyl substituted meso position. Thus, a mixing of distortion modes occurs in compounds of this type.

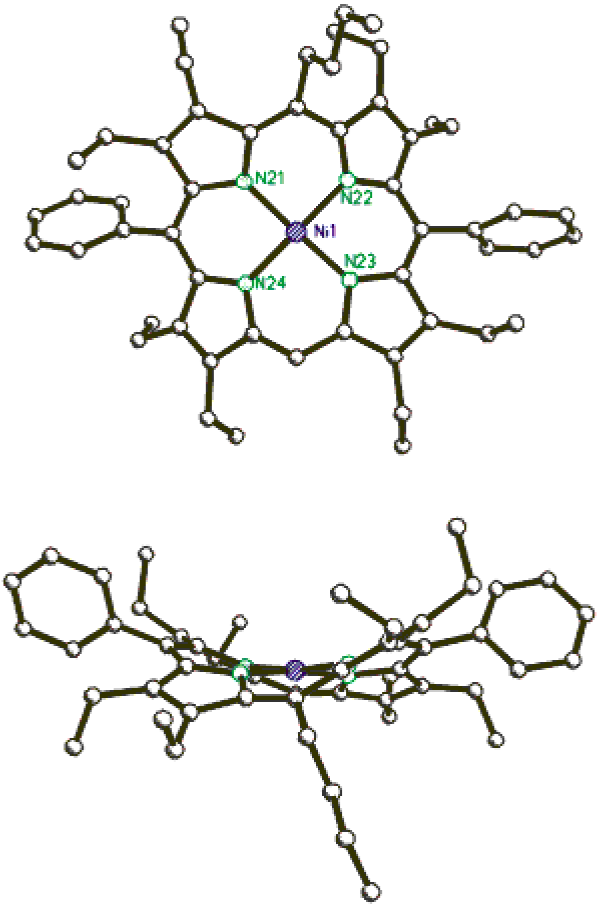
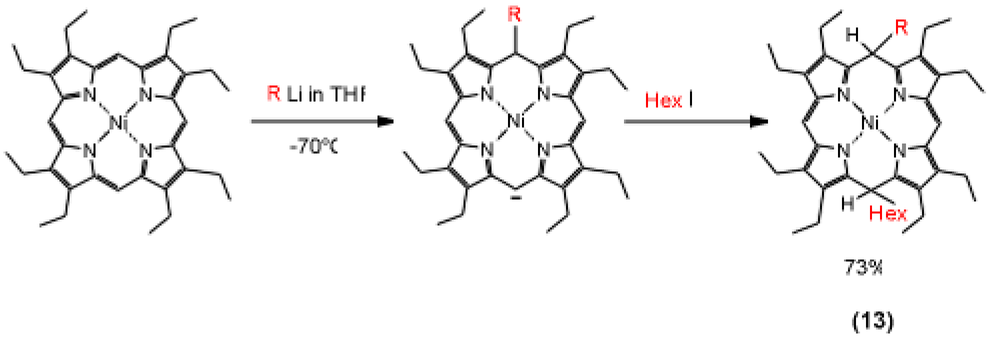


Fig. 1: Top and side view of the molecular structure of (5-butyl-2,3,7,8,12,13,17,18-octaethyl-10,20-diphenylporphyrinato)nickel(II).

Synthesis of Porphodimethenes

As described above treatment of NiOEP with BuLi gives an anion that potentially can be trapped with electrophiles. Thus, an alkyl iodide was added to the mixture containing the anionic species. When NiOEP was used as educt the reaction resulted in the formation of porphodimethenes (**13**), which could <u>not</u> be oxidized with DDQ, an indication of the validity of the proposed mechanism.



Scheme 5: Synthesis of a porphodimethene.

This method presents a general and efficient synthesis of stable porphodimethenes (Scheme 5). Using this method various porphodimethenes with butyl, hexyl, phenyl, propylcyanide, propyliodide, and hexylidode residues in different combinations were prepared in good to excellent yields. A crystal structure of one such stable porphodime-thene shows a *syn*-axial orientation of the meso hydrogen atoms (Figure 2).

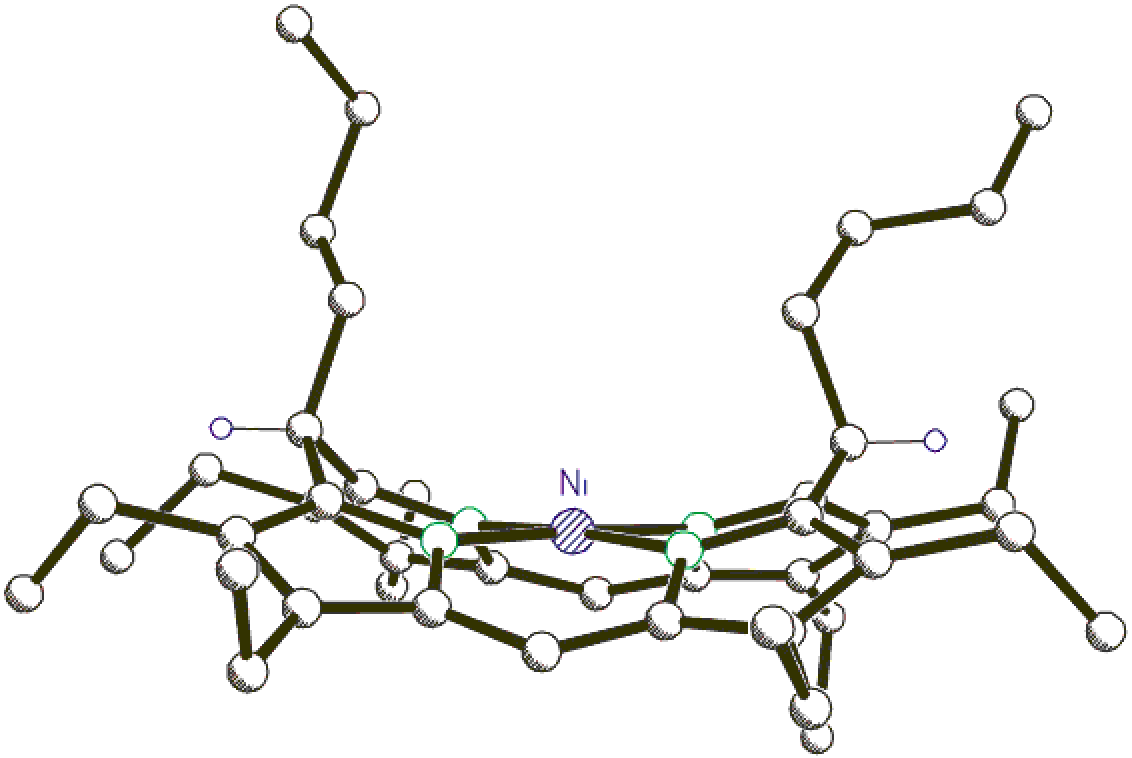


Fig. 2: Side view of the molecular structure of (5,15-dibutyl-2,3,7,8,12,13,17,18-octaethyl-5,15-dihydroporphyrinato)nickel(II).

Conclusion

The experiments have shown that the reaction of porphyrins with LiR introduces substituents at the meso position in an efficient and highly variable way. This method allows the facile synthesis of multiply meso substituted porphyrins and porphodimethenes in almost any desired regiochemical arrangement of the substitutents. Current studies are aimed at the investigation of the macrocycle conformation of these compounds by crystallographic means.

References

[1] [1a] S. Hanessian, G. McNaughton-Smith, H. G. Lomhart, W. D. Lubell, *Tetrahedron* **1997**, *53*, 12789-12854. G. D. Glick, *Biopolymers* **1998**, *48*, 83-96. R. W. Hoffmann, *Angew. Chem. Int. Ed.* **2000**, *39*, 2054-2070. J. A. Robinson, *Synlett* **2000**, 429-441. [1b] K. M. Barkigia, L. Chantranupong, K. M. Smith, J. Fajer, *J. Am. Chem. Soc.* **1988**, *110*, 7566–7567. – [1c] R. Huber, *Eur. J. Biochem.* **1990**, *187*, 283–305. M. O. Senge, *J. Photochem. Photobiol. B:Biol.* **1992**, *16*, 3–36. M. Ravikanth, T. K. Chandrashekar, *Struct. Bonding* **1995**, *82*, 105. J. Fajer, *J. Porphyrins Phthalocyanines* **2000**, *4*, 382–385.

[2] M. O. Senge, in *The Porphyrin Handbook* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, CA, **1999**, Vol. 1, p. 239–347.

[3] D. E. Tronrud, M. F. Schmid, B. W. Matthews, *J. Mol. Biol.* **1986**, *188*, 443–454. E. Gudowska-Novak, M. D. Newton, J. Fajer, *J. Phys. Chem.* **1990**, *94*, 5795–5801. S. M. Prince, M. Z. Papiz, A. A. Freer, G. McDermott, A. M. Hawthornwaite-Lawless, R. J. Cogdell, N. W. Isaacs, *J. Mol. Biol.* **1997**, *268*, 412–423.

[4] J. Deisenhofer, O. Epp, K. Mikki, R. Huber, H. Michel, *Nature*, **1985**, *318*, 618–624 J. P. Allen, G. Feher, T. P. Yeates, H. Komiya, R. C. Rees, *Proc. Natl. Acad. Sci. USA* **1987**, *84*, 5730–5734. M. Plato, K. Möbius, M. E. Michel-Beyerle, M. Bixon, J. Jortner, *J. Am. Chem. Soc.* **1988**, *110*, 7279–7285. J. R. Norris, D. E. Budil, P. Gast, C.-H. Chang, O. El-Kabbani, M. Schiffer, *Proc. Natl. Acad. Sci. USA* **1989**, *86*, 4335–4339. C. Kirmaier, D. Holten, *Proc. Natl. Acad. Sci. USA* **1990**, *87*, 3552–3556

[5] [5a] J. C. Kendrew, R. E. Dickerson, B. E. Strandberg, R. G. Hart, D. R. Davies, D. C. Philipps V. C. Shore, *Nature* **1960**, *185*, 422. T. Takano, *J. Mol. Biol.* **1977**, *110*, 537–568. A. Kuczera, J.-C. Lambry, J.-L. Martin, M. Karplus, *Proc. Natl. Acad. Sci. USA* **1993**, *90*, 5805–5807. [5b] Y. Higuchi, M. Kusunoki, Y. Matsuura, N. Yasuoka, M. Kakudo, *J. Mol. Biol.* **1984**, *172*, 109. G. R. Moore, G. W. Pettigrew, *Cytochromes c*. Springer-Verlag, Berlin, **1990**. M. E. P., Murphy, B. T. Nall, G. D. Brayer, *J. Mol. Biol.* **1992**, *227*, 160–176. [5c] T. L. Poulos, in *The Porphyrin Handbook* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, CA, **1999**, Vol. 4, p. 189–218. [5d] M. J. Mate, M. Zamocky, L. M. Nybyri, C. Herzog, P. M. Alzari, C. Betzel, F. Koller, I. Fita, *J. Mol. Biol.* **1999**, *268*, 135–149.

[6] A. M. Berghuis, G. D. Brayer, *J. Mol. Biol.* **1992**, *223*, 959–976. I. Schlichting, J. Berendzen, G. N. Phillips Jr., R. M. Sweet, *Nature* **1994**, *371*, 808–812. S. Othman, J. Fitch, M. A. Cusanowich, A. Desbois, *Biochemistry* **1997**, *36*, 5499–5508. I. Schlichting, J. Berendzen, K. Chu, A. M. Stock, *Science* **2000**, *287*, 1615-1622.

[7] [7a] M. K. Geno, J. Halpern, *J. Am. Chem. Soc.* **1987**, *109*, 1238. L. Furenlid, M. W. Renner, J. Fajer, *J. Am. Chem. Soc.* **1990**, *112*, 8987–8989. M. L. Ludwig, R. G. Matthews, *Annu. Rev. Biochem.* **1997**, *66*, 269–313. U. Ermler, W. Grabarse, S. Shima, M. Goubeaud, R. K. Thauer, *Science* **1997**, *278*, 1457–1462. [7b] C. Kratky, R. Waditschatka, C. Angst, P. E. Johansen, J. C. Plaquevent, J. Schreiber, A. Eschenmoser, *Helv. Chim. Acta* **1985**, *68*, 1312. [7c] B. R. Crane, L. M. Siegel, E. D. Getzoff, *Science*, **1995**, *270*, 59–67. P. A. Williams, V. Fülöp, E. F. Garman, N. F. W. Saunders, S. J. Ferguson, J. Hajdu, *Nature* **1997**, *389*, 406–412. D. Nurrizo, M.-C. Silvestrini, M. Mathieu, F. Cutruzzolà, D. Bourgeois, V. Fülöp, J. Hajdu, M. Brunori, M. Tegoni, C. Cambillau, *Structure* **1997**, *5*, 1158–1171.

[8] For a more complete discussion of the various biological examples and structural and spectroscopic evidence for the conformational control of biological reactions see references [1b,2,5c].

[9] K. J. Brunings, A. H. Corwin, *J. Am. Chem. Soc.* **1942**, *64*, 593. J. L. Hoard, *Ann. NY Acad. Sci.* **1973**, *206*, 18-31. M. B. Hursthouse, S. Neidle, *J. Chem. Soc., Chem. Commun.* **1972**, 449. J.-H. Fuhrhop, L. Witte, W. S. Sheldrick, *Liebigs Ann. Chem.* **1976**, 1537.

[10] [10a] D. Dolphin, *J. Heterocycl. Chem.* **1970**, *7*, 275. K. M. Barkigia, M. D. Berber, J. Fajer, C. J. Medforth, M. W. Renner, K. M. Smith, *J. Am. Chem. Soc.* **1990**, *112*, 8851–8857. J. A. Shelnutt, C. J. Medforth, M. D. Berber, K. M. Barkigia, K. M. Smith, *J. Am. Chem. Soc.* **1991**, *113*, 4077–4087. L. D. Sparks, C. J. Medforth, M.-S. Park, J. R. Chamberlain, M. R. Ondrias, M. O. Senge, K. M. Smith, J. A. Shelnutt, *J. Am. Chem. Soc* **1993**, *115*, 581–592. M. W. Renner, K. M. Barkigia, Y. Zhang, C. J. Medforth, K. M. Smith, J. Fajer, *J. Am. Chem. Soc.* **1994**, *116*, 8582–8592. S. Gentemann, C. J. Medforth, T. P. Forsyth, D. J. Nurco, K. M. Smith, J. Fajer, D. Holten, *J. Am. Chem. Soc.* **1994**, *116*, 7363–7368. K. M. Kadish, E. Van Caemelbecke, F. D'Souza, C. J. Medforth, K. M. Smith, A. Tabard, R. Guilard, *Inorg. Chem.* **1995**, *34*, 2984–2989. M. O. Senge, W. W. Kalisch, S. Runge, *Liebigs Ann.* **1997**, 1345–1352. R.-J. Cheng, P.-Y. Chen, P.-R. Gau, S.-M. Peng, *J. Am. Chem. Soc.* **1997**, *119*, 2563–2569. [10b] K. M. Barkigia, M. W. Renner, L. R. Furenlid, C. J. Medforth, K. M. Smith, J. Fajer, *J. Am. Chem. Soc* **1993**, **115**, 3627–3635. M. O. Senge, C. J. Medforth, L. D. Sparks, J. A. Shelnutt, K. M. Smith, *Inorg. Chem.* **1993**, *32*, 1716–1723. L. D. Sparks, K. K. Anderson, C. J. Medforth, K. M. Smith, J. A. Shelnutt, *Inorg. Chem.* **1994**, *32*, 2297–2302. [10c] M. O. Senge, T. P. Forsyth, L. T. Nguyen, K. M. Smith, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2485–2487. M. O. Senge, W. W. Kalisch, *Z. Naturforsch.* **1999**, *54b*, 943–959. [10d] X. Zhou, M. K. Tse, T. S. M. Wan, K. S. Chan, *J. Org. Chem.* **1996**, *61*, 3590–3593.

[11] [11a] S. Tsuchiya, *Chem. Phys. Lett.* **1990**, *169*, 608–610; *J. Chem. Soc., Chem. Commun.* **1992**, 1475–1477. C. J. Medforth, K. M. Smith, *Tetrahedron Lett.* **1990**, *31*, 5583–5586. J. Takeda, T. Ohya, M. Sato, *Inorg. Chem.* **1992**, *31*, 2877–2880. J. Takeda, M. Sato, *Chem. Lett.* **1995**, 939–940; 971–972. D. J. Nurco, C. J. Medforth, T. P. Forsyth, M. M. Olmstead, K. M. Smith, *J. Am. Chem. Soc.* **1996**, *118*, 10918–10919. K. Perié, J.-M. Barbe, P. Cocolios, R. Guilard, *Bull. Soc. Chim. Fr.* **1996**, *113*, 697–702. R. Guilard, K. Perié, J.-M. Barbe, D. J. Nurco, K. M. Smith, E. Van Caemelbecke, K. M. Kadish, *Inorg. Chem.* **1998**, *37*, 973–981. N. Ono, H. Miyagawa, T. Ueta, T. Ogawa, H. Tani, *J. Chem. Soc., Perkin Trans. 1* **1998**, 1595–1601. C.-J. Liu, W.-Y. Yu, S.-M. Peng, T. C. W. Mak, C.-M. Che, *J. Chem. Soc., Dalton Trans.* **1998**, 1805–1812. M. O. Senge, *Z. Naturforsch.* **1999**, *54b*, 821-824. C. M. Muzzi, C. J. Medforth, L. Voss, M. Cancilla, C Lebrilla, J.-G. Ma, J. A. Shelnutt, K. M. Smith, *Tetrahedron Lett.* **1999**, *40*, 6159-6162. [11b] C. J. Medforth, M. O. Senge, K. M. Smith, L. D. Sparks, J. A. Shelnutt, *J. Am. Chem. Soc.* **1992**, *114*, 9859–9869.

[12] J. C., Fanning, T. L. Gray, N. Datta-Gupta, *J. Chem. Soc., Chem. Commun.* **1974**, 23.

[13] [13a] W. W. Kalisch, M. O. Senge, *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 1107–1109. M. O. Senge, W. W. Kalisch, I. Bischoff, *Chem. Eur. J.* **2000**, in press. [13b] M. O. Senge, M. W. Renner, W. W. Kalisch, J. Fajer, *J. Chem. Soc., Dalton Trans.* **2000**, 381-385.

[14] [14a] D. Mandon, P. Ochsenbein, J. Fischer, R. Weiss, K. Jayaraj, R. N. Austin, A. Gold, P. S. White, O. Brigaud, P. Battioni, D. Mansuy, *Inorg. Chem.* **1992**, *31*, 2044–2049. P. Bhyrappa, V. Krishnan, M. Nethaji, *J. Chem. Soc., Dalton Trans.* **1993**, 1901–1906. P. Bhyrappa, M. Nethaji, V. Krishnan, *Chem. Lett.* **1993**, 869–872. P. Ochsenbein, D. Mandon, J. Fischer, R. Weiss, R. Austin, K. Jayaraj, A. Gold, J. Terner, E. Bill, M. Müther, A. X. Trautwein, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1437–1439. E. R. Birnbaum, J. A. Hodge, M. W. Grinstaff, W. P. Schaefer, L. Henling, J. A. Labinger, J. E. Bercaw, H. B. Gray, *Inorg. Chem.* **1995**, *34*, 3625–3632. M. W. Grinstaff, M. G. Hill, E. R. Birnbaum, W. P. Schaefer, J. A. Labinger, H. B. Gray, *Inorg. Chem.* **1995**, *34*, 4896–4902. K. M. Kadish, J. Li, E. Van Caemelbecke, Z. Ou, N. Guo, M. Autret, F. D'Souza, P. Tagliatesta *Inorg. Chem.* **1997**, *36*, 6292–6298. G. A. Spyroulias, A. Despotopoulos, C. P. Raptopoulou, A. Terzis, A. G. Coutsolelos, *Chem. Commun.* **1997**, 783–784. J. Leroy, A. Bondon, L. Toupet, C. Rolando, *Chem. Eur. J.* **1997**, *3*, 1890–1893. E. K. Woller, S. G. DiMagno, *J. Org. Chem.* **1997**, *62*, 1588–1593. [14b] D. Dolphin, T. D. Traylor and L. Y. Xie, *Acc. Chem. Res.* **1997**, *30*, 251–259. B. Meunier, A. Robert, G. Pratviel, J. Bernadou, in *The Porphyrin Handbook* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, CA, **1999**, Vol. 4, p. 119–187.

[15] [15a] T. Ema, M. O. Senge, N. Y. Nelson, H. Ogoshi, K. M. Smith, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1879–1881. M. O. Senge, T. Ema, K. M. Smith, *Chem. Commun.* **1995**, 733–734. W. Jentzen, M. C. Simpson, J. D. Hobbs, X. Song, T. Ema, N. Y. Nelson, C. J. Medforth, K. M. Smith, M. Veyrat, M. Mazzanti, R. Ramasseul, J.-C. Marchon, T. Takeuchi, W. A. Goddard, J. A. Shelnutt, *J. Am. Chem. Soc.* **1995**, *117*, 11085–11097. M. O. Senge, I. Bischoff, N. Y. Nelson, K. M. Smith, *J. Porphyrins Phthalocyanines* **1999**, *3*, 99–116. M. O. Senge, *Z. Naturforsch.* **2000**, *55b*, 336-344. [15b] M. Onaka, T. Shinoda, Y. Izumi, E. Nolen, *Chem. Lett.* **1993**, 117–120. M. Mazzanti, J.-C. Marchon, M. Shang, W. R. Scheidt, S. Jia, J. A. Shelnutt, *J. Am. Chem. Soc.* **1997**, *119*, 12400–12401. D. Toronto, F. Sarrazin, J. Pécaut, J.-C. Marchon, M. Shang, W. R. Scheidt, *Inorg. Chem.* **1998**, *37*, 526–532. S. Runge, M. O. Senge, K. Ruhlandt-Senge, *Z. Naturforsch.* **1999**, *54b*, 662-666. [15c] C.-Y. Lin, S. Hu, T. Rush III, T. G. Spiro, *J. Am. Chem. Soc.* **1996**, *118*, 9452–9453. C. M. Drain, S. Gentemann, J. A. Roberts, N. Y. Nelson, C. J. Medforth, S. Jia, M. C. Simpson, K. M. Smith, J. Fajer, J. A. Shelnutt, D. Holten, *J. Am. Chem. Soc.* **1998**, *120*, 3781–3791. M. S. Somma, C. J. Medforth, N. Y. Nelson, M. M. Olmstead, R. G. Khoury, K. M. Smith, *Chem. Commun.* **1999**, 1221–1222.

[16] J. S. Lindsey, in *The Porphyrin Handbook* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, CA, **1999**, Vol. 1, p. 45–118.

[17]M. O. Senge, X. Feng, *Tetrahedron Lett.* **1999**, *40*, 4165-4168.

[18] For related studies on the reactivity of other tetrapyrroles with LiR see: B. Krattinger, H. J. Callot, *Tetrahedron Lett.*, **1996**, *37*, 7699–7702; **1998**, *39*, 1165–1168; *Eur. J. Org. Chem.* **1999**, 1857–1867. L. Bonomo, E. Solari, R. Scopelliti, C. Floriani, N. Re, *J. Am. Chem. Soc.* **2000**, *122*, 5312-5326.

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