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PORPHYRIN DERIVATIVES-PROPERTIES AND APPLICATIONS

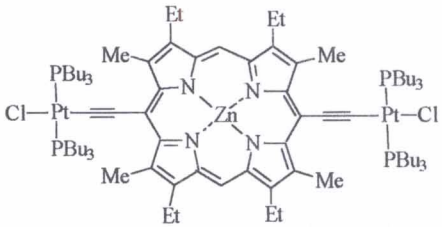
Abstract: In the paper structure and properties of chosen porphyrin derivatives are presented, along with possibilities of their applications.

Introduction

Porphyrins, large aromatic macrocycles are a topic of intensive study due to their interesting properties [1-10]. These species play an important role in biological processes and are promising for use in optoelectronic devices and in the construction of organic solar cells. In the paper chosen examples of porphyrin derivatives are presented.

Porphyrin derivatives

To porphyrins possessing in their structure besides zinc as central metal atom the platinum complexes at *meso* positions belong macrosystems 1 and 2; their electronic and conformational characterization has been made with the use of X-ray photoelectron spectroscopy [11].



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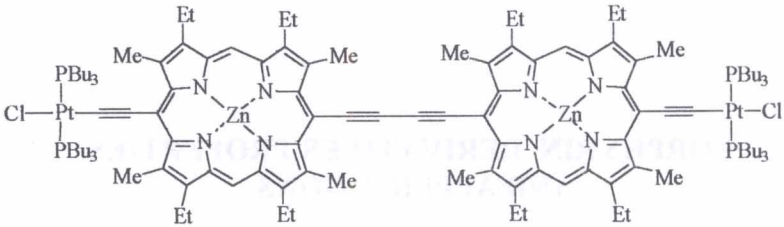

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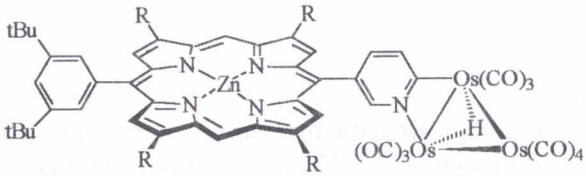
Examples of multimetallic porphyrins are compounds 3 - 5. In the case of 5 the exchange between *cis* and *trans* isomeric forms occurs, as was shown by ^{1}H NMR spectral results [12,13].



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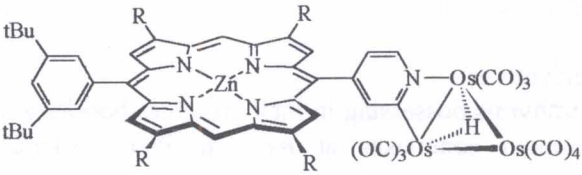

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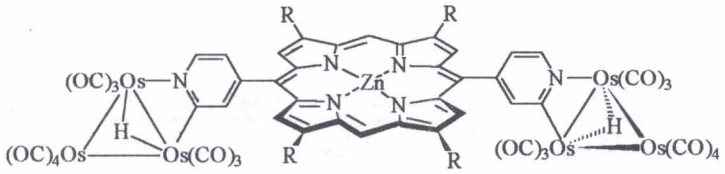
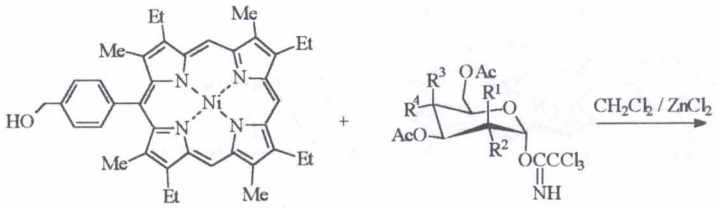


R = nC_6H_{13} 5

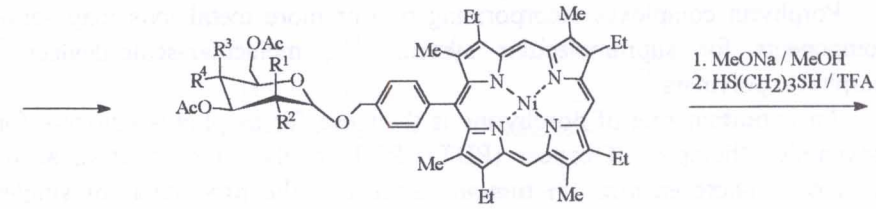
Porphyrin complexes incorporating two or more metal ions may serve as components for supramolecular systems [14,15], molecular-scale devices [16] and porphyrin polymers [17].

An important role of porphyrins is their use for as photosensitizers for photodynamic therapy of cancer (PDT). PDT involves the selective accumulation of a photosensitizer in tumour tissue and the production of singlet oxygen by irradiation with visible light leading to the destruction of tumour cells.

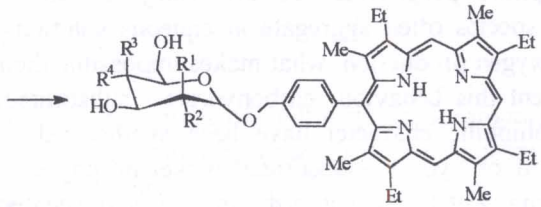
Hydrophobic and amphiphilic porphyrins are promising for photodynamic therapy. However these species often aggregate in aqueous solutions, thus decreasing ability to singlet oxygen production, what makes impossible their use in PDT. In order to circumvent this behaviour carbohydrate - substituted, water soluble porphyrins of amphiphilic character have been synthesized [18]. The synthesis involves the reaction of hydroxy-substituted nickel porphyrin 7 with glycosyl imidates 8a-g using $ZnCl_2$ as catalyst. In the glycosylated compounds 9 the acetal groups were removed by treatment with sodium methanolate, and after demetallation with propanedithiol/ TFA the carbohydrate substituted porphyrins 10 have been obtained. Interesting properties of 10 concerning PDT have been found [18].



7 8a-g



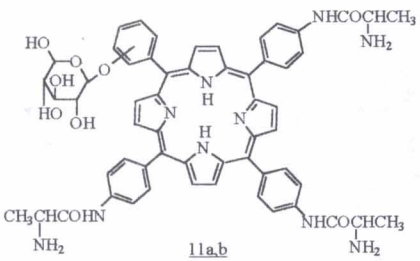
9a-g



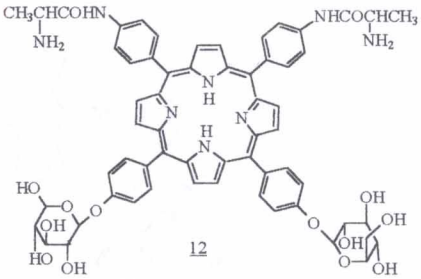
10a-g

	R1	R2	R3	R4
8a	OAc	H	H	OAc
8b	H	OAc	OAc	H
8c	H	OAc	H	OAc
8d	H	NHAc	H	OAc
8e	H	OAc	H	α(1,4)Glc(OAc)4
8f	H	OAc	H	β(1,4)Gal(OAc)4
8g	H	OAc	H	β(1,4)Glc(OAc)4
10a	OH	H	H	OH
10b	H	OH	OH	H
10c	H	OH	H	OH
10d	H	NHAc	H	OH
10e	H	OH	H	α(1,4)Glc
10f	H	OH	H	β(1,4)Gal
10g	H	OH	H	β(1,4)Glc

In the search for convenient PDT photosensitizers also glycosylated amino acid porphyrins 11 - 15 have been synthesized and their photocytotoxicity tested. Compounds 11 - 14 bear alanyl groups in the *ortho* or *para* positions of the *meso* phenyl, while in 15a,b the glycosyl moiety is separated from porphyrin molecule by a serine unit [19-23].



11a,b



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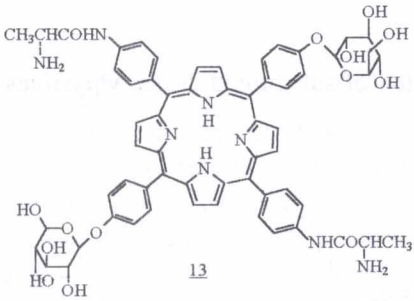

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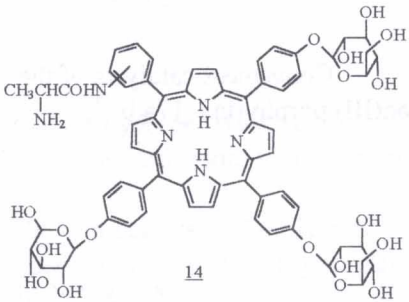

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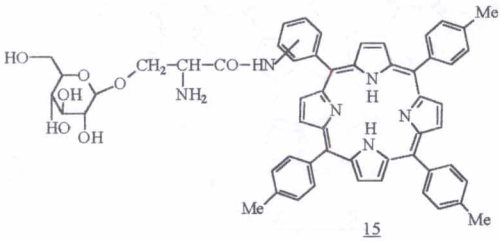
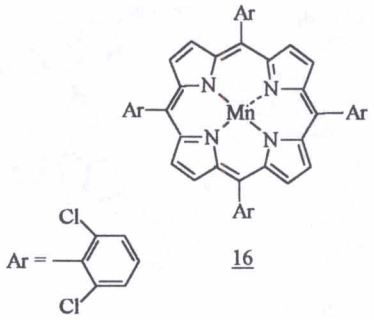


a = *ortho-*
b = *para-*

15

The investigations have shown that compounds 11 - 14 produce singlet oxygen almost as efficiently as hematoporphyrin, which is a good photosensitizer. The photocytotoxicity of 12 , 13 and 14a against K 562 when irradiation was longer than 60 min, was comparable to that of hematoporphyrin.

Porphyrins often are used as catalysts, e.g. 16 catalyzes naphthalene oxidation by peracetic acid. In the study of mechanism of this process it was observed that the nature of products depends on the catalyst structure [24].



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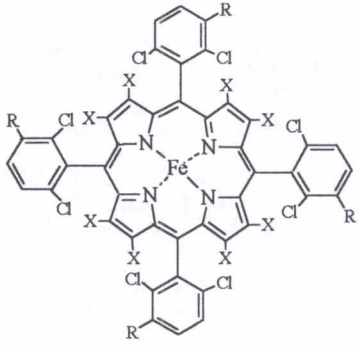
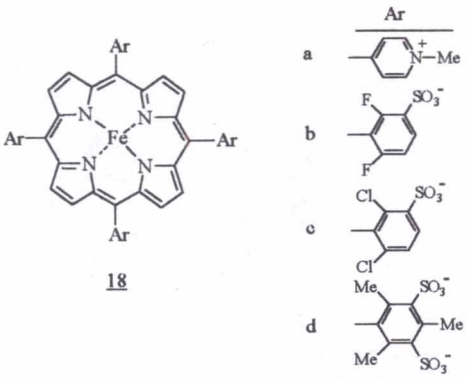
Convenient catalysts of the oxidation of substituted 2-methylpyrroles are iron(III) porphyrins 17a,b [25].



		R	X
17	a	H	Cl
	b	SO_3H	Cl

Porphyrins 18a-d have been used as catalysts of the stilbene epoxidation with 2-methyl-1-phenylpropan-2-yl hydroperoxide 19 serving as oxidant, and the mechanism of the O-O bond cleavage of 19 has been investigated [26-29].

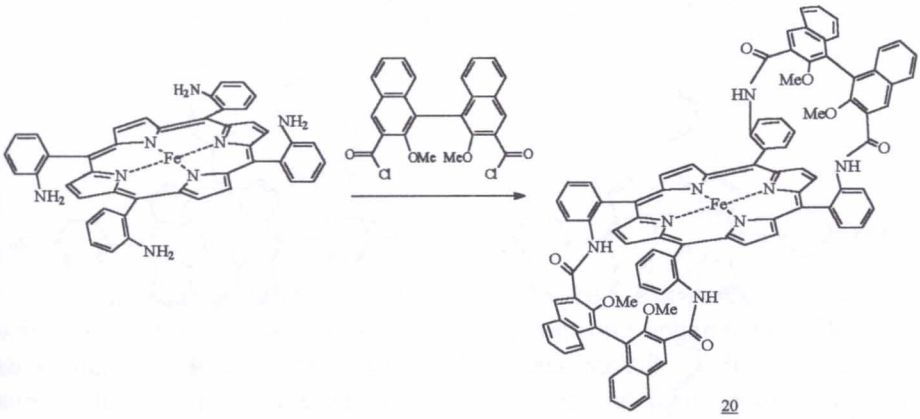


18

It was found that the O-O bond of *tert*-alkyl hydroperoxides is cleaved both heterolytically and homolytically, depending on the electronic nature of the porphyrin and the reaction pH [26].

An example of a chiral porphyrin serving as a catalyst is 20. This compound gives very high ee values and turnover numbers for asymmetric epoxidation of terminal alkenes and styrene derivatives [30].

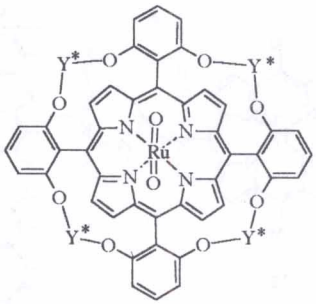
Porphyrin 20 is ready available by the following procedure:



20

In these reactions iodosylbenzene served as an oxidant, and investigated alkenes were 3,3-dimethylbutene, styrene, *m*-chlorostyrene and pentafluorostyrene [30].

It was established that D_2-symmetric chiral dioxoruthenium(VI) porphyrins catalyze enantioselective epoxidation of *trans*-disubstituted alkenes; for example 21 effects enantioselective epoxidation of *trans*-β-methylstyrene in up to 70% ee [31,32].



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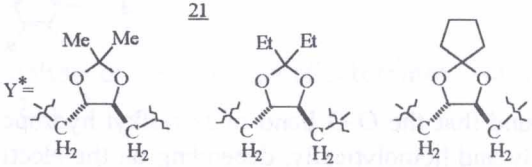
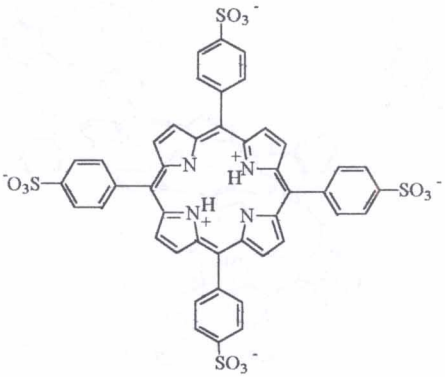


Chiral ternary complexes of 22 on a preformed complex between 23 and α-helical polyglutamate have been studied by UV, fluorescence and CD spectroscopy in aqueous solution [33,34]. This complex is an interesting example of porphyrin assemblies which do not follow the "chirality" of the template they were grown on.



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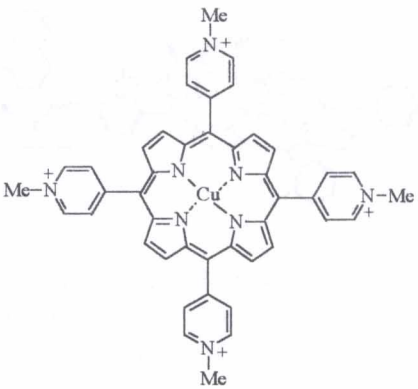
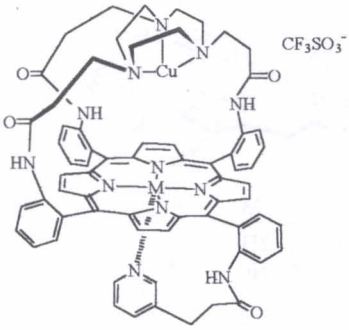
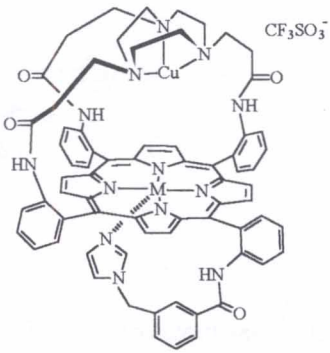


23

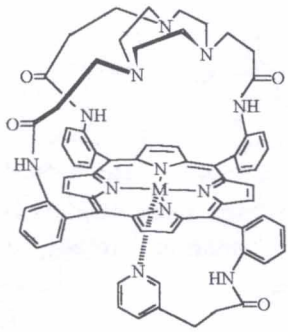
In the study of model compounds for Fe_{a3}/Cu_B active site of cytochrome c oxidase, Zn(II)/Cu(I) 24a , 25a and Fe(II)/Cu(I) 24b , 25b complexes have been synthesized [35-37]. The first step of the synthesis is the metallation of the TACN capped free base porphyrins 26 and 27 into 26b,c and 27b,c using zinc acetate and $FeBr_2$, respectively (TACN= 1,4,7-triazacyclononane). Treatment of 26b,c and 27b,c with copper(I) triflate affords 24a,b and 25a,b.



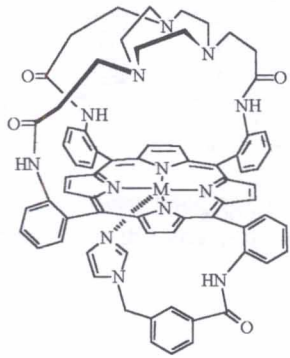
24 M: a Zn; b Fe



25 M: a Zn; b Fe



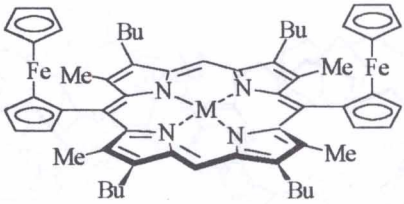
26 M: a 2H; b Zn; c Fe



27 M: a 2H; b Zn; c Fe

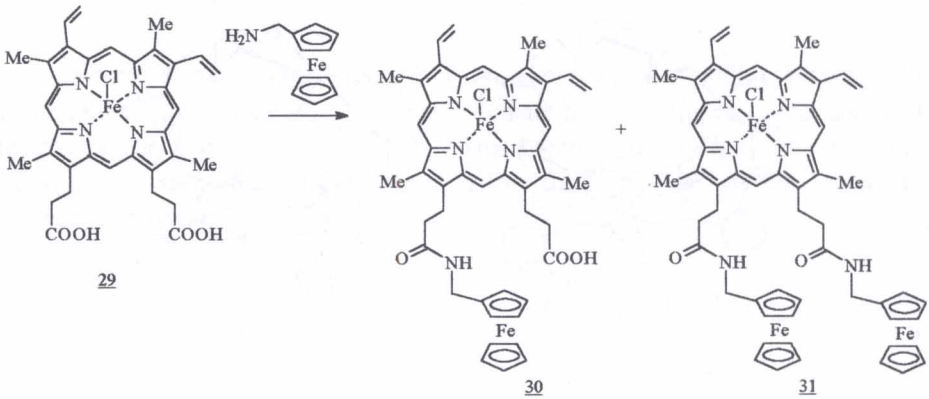
The electrocatalytic reduction of O_2 by Fe/Cu complexes 24b and 25b was examined by rotating graphite disc-platinum ring voltammetry. The results show that these species are convenient functional models for the Fe_{a3}/Cu_B active sites of heme-copper oxidases; an advantage is that their catalytic properties may be tuned by small structural changes in the porphyrin macrocycle. [35]

Bis(ferrocenyl)porphyrin 28a has been obtained by the condensation of tetraalkyl dipyrromethane and ferrocene aldehyde; its metallation afforded 28b. The reaction leads to a single atropoisomer αα, the αβ isomer is not formed. It was established that in both 28a and 28b the macrocycle is ruffled [38,39].

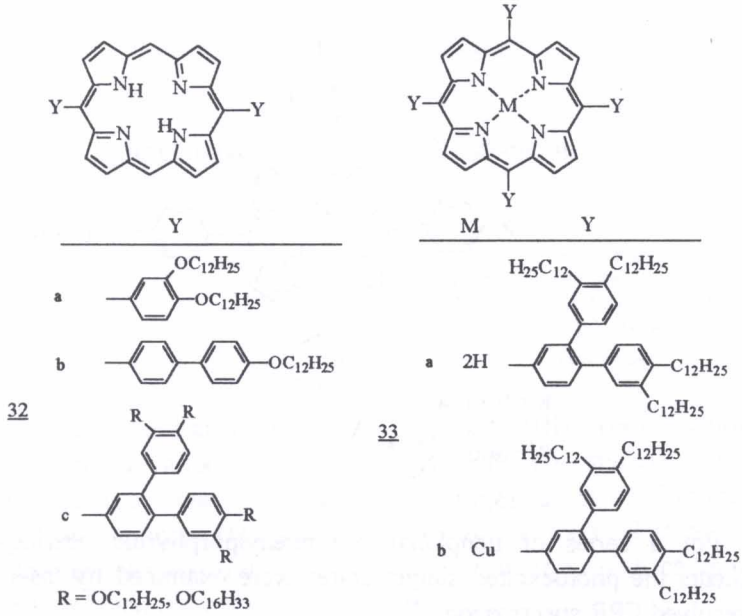


	M
28 a	2H
b	Ni

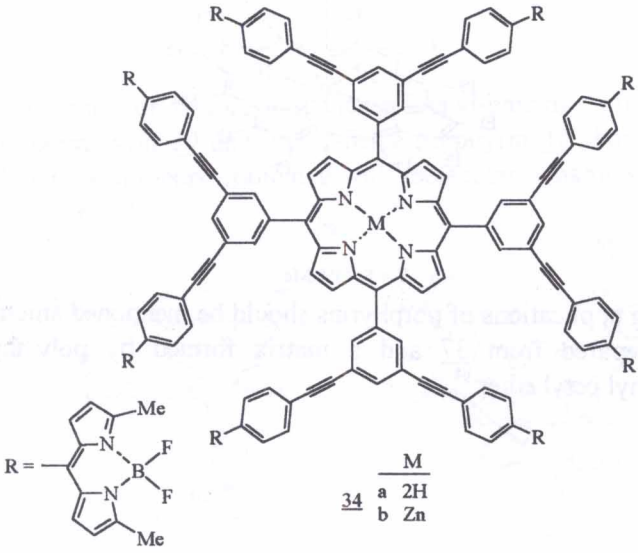
Following modifications of hemin chloride 29 by aminomethylferrocene leading to 30 and 31 have been performed [40].

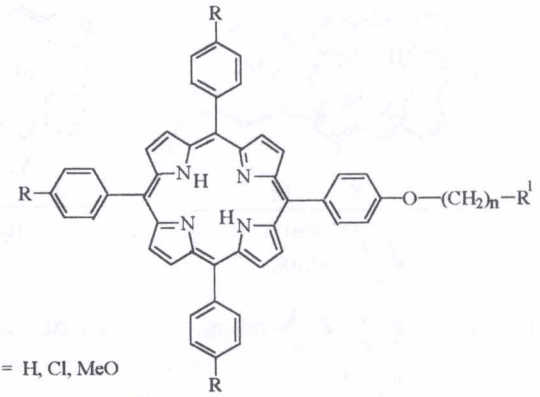


Porphyrin derivatives substituted with bulky groups 32a-c and 33a,b have been synthesized in order to investigate the relationship between the nature of substitution and the resulting mesophase [41].



MALDI-TOF mass spectrometry [42] has been used for characterization of porphyrins 34a,b [43], and the ^{1}H NMR data for the analysis of compounds 35 [44,45].





R = H, Cl, MeO

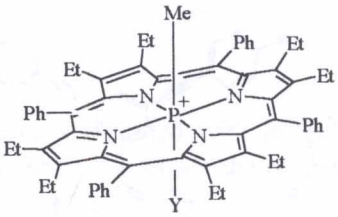
$R^1 = \overset{+}{N}Et_3$, 

n = 2,3,4

35

For a series of nonplanar tetraphenylporphyrins bearing peripheral substituents the photoexcited singlet states were examined by laser excitation--time-resolved EPR spectroscopy [46].

In the X-ray crystallographic study of phosphorus porphyrins 36 it was established that the axial ligand plays an important role in changing the conformation of the porphyrin core from ruffled one (Y=F, OH) into saddle (Y=Me) [47].



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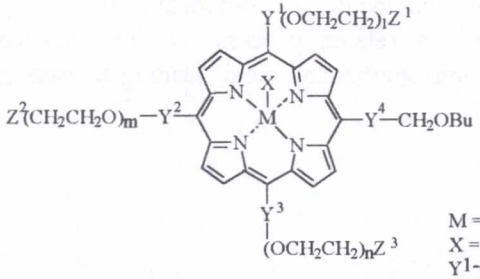
Y = F, OH, Me

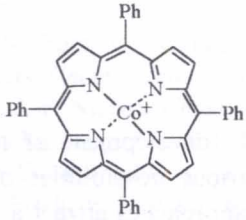
Among applications of porphyrins should be mentioned anion responsive membranes prepared from 37 and a matrix formed by polyvinyl chloride and *o*-nitrophenyl octyl ether [48].



37

M = Mn, In
X = halo
Y1-4 = alkylene, phenylene
Z 1-3 = H, alkyl
l,m,n, = 2-6

The one-electron transfer in the reduction of Co(III) tetraphenylporphyrin 38 incorporated into a Nafion or poly(4-vinyl)pyridine - *co* - styrene film coated on an ITO electrode was investigated by potential step chronoampero-spectrometry measurements (ITO electrode = indium tin oxide electrode). It was established that the electron transfer of the redox centers in both cases occured *via* a physical diffusion mechanism [49].



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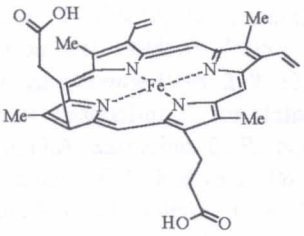
In the study of factors influencing ligand-binding properties of heme models, protoporphyrin 39 and picket-fence porphyrin 40 have been analyzed by density functional theory combined with molecular dynamics within the Car-Parrinello scheme [50,51].



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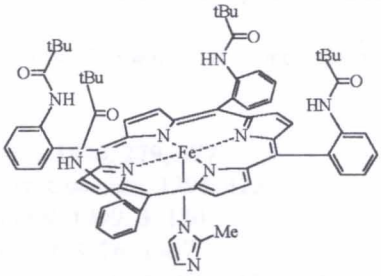

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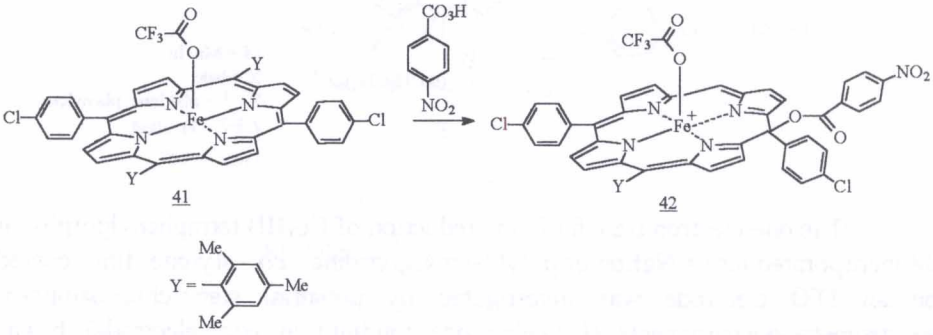
In order to elucidate *meso*-hydroxylation of porphyrin catalyzed by heme oxygenase , a related process, i.e. *meso*-oxygenation of the iron porphyrin 41 with *p*-nitroperbenzoic acid, leading to isoporphyrin 42 has been performed [52].



Conclusion

At present a rapid development of research concerning porphyrin derivatives is observed. Various possibilities of their applications along with rather convenient synthetic approaches attract a considerable attention, what has its reflection in an increasing number of new reports on this theme. [53-60]

REFERENCES

1. K.M. Kadish, Z. Ou, X. Tan, T. Boschi, D. Monti, V. Fares, P. Tagliatesta, *J. Chem. Soc.,Dalton Trans.* 1999, 1595
2. B. Venkatesh, S. Ramasamy, M. Mylrajan, R. Asokan, P.T. Manoharan, J.M. Rifkind, *Spectrochim. Acta A,* 1999, **55**, 1691
3. D.J. Fermin, H.D. Duong, Z. Ding, P.-F. Brevet, H.H. Girault, *Phys. Chem. Chem. Phys.* 1999, **1**, 1461
4. R. Rubires, J. Crusats, Z. El-Hachemi, T. Jaramillo, M. Lopez, E. Valls, J.-A. Farrera, J.M. Ribo, *New J. Chem.* 1999, **23**, 189
5. M. Dudič, P. Lhoták, V. Král, K. Lang, I. Stibor, *Tetrahedron Lett.* 1999, **40**, 5949
6. L.J. Twyman, J.K.M. Sanders, *Tetrahedron Lett.* 1999, **40**, 6681
7. J.N.H. Reek, A.E. Rowan, M.J. Crossley, R.J.M. Nolte, *J. Org. Chem.* 1999, **64**, 6653
8. W. Śliwa, B. Mianowska, *Transition Metal Chem.*, in press
9. W. Śliwa, *Porphyrins and Related Compounds,* Pedagogical University, Częstochowa, in press
10. W. Śliwa, *Chemia, Dydaktyka, Ekologia, Metrologia,* Tow. Chemii i Inżynierii Ekologicznej, Opole, in press
11. G. Polzonetti, A. Ferri, M.V. Russo, G. Iucci, S. Licoccia, R. Paolesse, *J. Vac. Sci. Technol. A,* 1999, **17**, 832
12. S.L. Darling, P.K.Y. Goh, N. Bampos, N. Feeder, M. Montalti, L. Prodi, B.F.G. Johnson, J.K.M. Sanders, *Chem. Commun.* 1998, 2031
13. J.-F. Nierengarten, L. Oswald, J.-F. Nicoud, *Chem. Commun.* 1998, 1545
14. N. Kariya, T. Imamura, Y. Sasaki, *Inorg. Chem.* 1998, **37**, 1658
15. K.M. Kadish, N. Guo, E. Van Caemelbecke, A. Froiio , R. Paolesse, D. Monti, P. Tagliatesta, T. Boschi, L. Prodi, F. Bolletta, N. Zaccheroni, *Inorg. Chem.* 1998, **37**, 2358
16. L. Jaquinod, O. Siri, R.G. Khoury, K.M. Smith, *Chem. Commun.* 1998, 1261
17. P.N. Taylor, J. Huuskonen, G. Rumbles, R.T. Aplin, E. Williams, H.L. Anderson, *Chem. Commun.* 1998, 909
18. Ch. Schell, H.K. Hombrecher, *Chem. Eur. J.* 1999, **5**, 587
19. V. Sol, J.C. Blais, V. Carré, R. Granet, M. Guilloton, M. Spiro, P. Krausz, *J. Org. Chem.*1999, **64**, 4431
20. Y. Mikata, Y. Onchi, K. Tabata, S. Ogura, I. Okura, H. Ono, S. Yano, *Tetrahedron Lett.* 1998, **39**, 4505
21. M. Barinaga, *Science* 1998, **279**, 323
22. W. Arap, R. Pasqualini, E. Ruoslahti, *Science* 1998, **279**, 377
23. R.K. Jain, D.A. Sarracino, C. Richert, *Chem. Commun.* 1998, 423
24. S.V. Barkanova, O.L. Kaliya, *J. Porph. Phthal.* 1999, **3**, 180
25. V. Karunaratne, D. Dolphin, *Can. J. Chem.* 1998, **76**, 1467
26. W. Nam, H.J. Choi, H.J. Han, S.H. Cho, H.J. Lee, S.-Y. Han, *Chem. Commun.* 1999, 387
27. P.A. MacFaul, D.D.M. Wayner, K.U. Ingold, *Acc. Chem. Res.* 1998, **31**, 159

28. A. Hadasch, A. Sorokin, A. Rubion, B. Meunier, *New J. Chem.* 1998, 45
29. S.J. Yang, W. Nam, *Inorg. Chem.* 1998, **37**, 606
30. J.P. Collman, Z. Wang, A. Straumanis, M. Quelquejeu, *J. Am. Chem. Soc.* 1999, **121**, 460
31. R. Zhang, W.-Y. Yu, T.-S. Lai, Ch.-M. Che, *Chem. Commun.* 1999, 409
32. W.-H. Fung, W.-Y. Yu, C.-M. Che, *J. Org. Chem.* 1998, **63**, 7715
33. E. Bellacchio, R. Lauceri, S. Gurrieri, L.Monsů Scolaro, A. Romeo, R. Purrello, *J. Am. Chem. Soc.* 1998, **120**, 12353
34. R. Purrello, L. Monsů Scolaro, E. Bellacchio, S. Gurrieri, A. Romeo, *Inorg. Chem.* 1998, **37**, 3647
35. J.P. Collman, R. Schwenninger, M. Rapta, M. Bröring, L. Fu, *Chem. Commun.* 1999, 137
36. J.P. Collman, M. Bröring, L. Fu, M. Rapta, R. Schwenninger, A. Straumanis, *J. Org. Chem.* 1998, **63**, 8082
37. J.P. Collman, M. Bröring, L. Fu, M. Rapta, R. Schwenninger, *J. Org. Chem.* 1998, **63**, 8084
38. P.D.W. Boyd, A.K. Burrell, W.M. Campbell, P.A. Cocks, K.C. Gordon, G.B. Jameson, D.L. Officer, Z. Zhao, *Chem. Commun.* 1999, 637
39. C. Patoux, J.-P. Launay, M. Beley, S. Chodorowski-Kimmes, J.-P. Collin, S. James, J.-P. Sauvage, *J. Am. Chem. Soc.* 1998, **120**, 3717
40. A.D. Ryabov, V.N. Goral, L. Gorton, E. Csöregi, *Chem. Eur. J.* 1999, **5**, 961
41. K. Ohta, N. Yamaguchi, I. Yamamoto, *J. Mater. Chem.* 1998, **8**, 2637
42. N. Srinivasan, C.A. Haney, J.S. Lindsey, W. Zhang, B.T. Chait, *J. Porph. Phthal.* 1999, **3**, 283
43. F. Li, S.I. Yang, Y. Ciringh, J. Seth, C.H. Martin III, D.L. Singh, D. Kim, R.R. Birge,D.F. Bocian, D. Holten, J.S. Lindsey, *J. Am. Chem. Soc.* 1998, **120**, 10001
44. Q. Yang, S. Han, Y. Liu, K. Hou, *Bopuxue Zazhi* 1999, 16, 83; *Chem Abstr.* 1999, **131**, 5136
45. Q. Yang, S. Han, Y. Liu, K. Hou, *Bopuxue Zazhi* 1999, 16, 77; *Chem. Abstr.* 1999, **131**, 5135
46. S. Michaeli, S. Soffer, H. Levanon, M.O. Senge, W.W. Kalisch, *J. Phys. Chem. A*, 1999, **103**, 1950
47. A. Yamamoto, W. Satoh, Y. Yamamoto, K. Akiba, *Chem. Commun.* 1999, 147
48. H. Taira, K. Matsuuchi, H. Yanagi, Jpn. Kokai Tokkyo Koho JP 09,249,670 (1997); *Chem. Abstr.* 1997, **127**, 358748
49. F. Zhao, J. Zhang, T. Abe, M. Kaneko, *J. Porph. Phthal.* 1999, **3**, 238
50. C. Rovira, M. Parrinello, *Chem. Eur. J.* 1999, **5**, 250
51. C. Rovira, M. Parrinello, *Int. J. Quant. Chem.* 1998, **70**, 387
52. T. Murakami, Y. Watanabe, I. Morishima, *Chem. Lett.* 1998, 27
53. K. Konishi, M. Suezaki, T. Aida, *Tetrahedron Lett.* 1999, **40**, 6951
54. E. Baciocchi, A. Lapi, *Tetrahedron Lett.* 1999, **40**, 5425
55. A. Ando, M. Yamazaki, M. Komura, Y. Sano, N. Hattori, M. Omote, I. Kumadaki, *Heterocycles* 1999, **50**, 913

56. L. Latterini, R. Blossey, J. Hofkens, P. Vanoppen, F. C. De Schryver, A.E. Rowan, R.J.M. Nolte, *Langmuir* 1999, **15**, 3582
57. 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
58. H. Tamiaki, M. Onishi, *Tetrahedron : Asymmetry* 1999, **10**, 1029
59. M.R.M. Domingues, M.G. Santana-Marques, A.J. Ferrer-Correia, A.C. Tome, M.G.P.M.S. Neves, J.A.S. Cavaleiro, *J. Porph. Phthal.* 1999, **3**, 172
60. H.-Z. Yu, J.S. Baskin, B. Steiger, F.C. Anson, A.H. Zewail, *J. Am. Chem. Soc.* 1999, **121**, 484

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Pochodne porfiryn - właściwości i zastosowania

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