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Synthesis of N,N'-Etheno-Bridged Porphycene Hydroperchlorates

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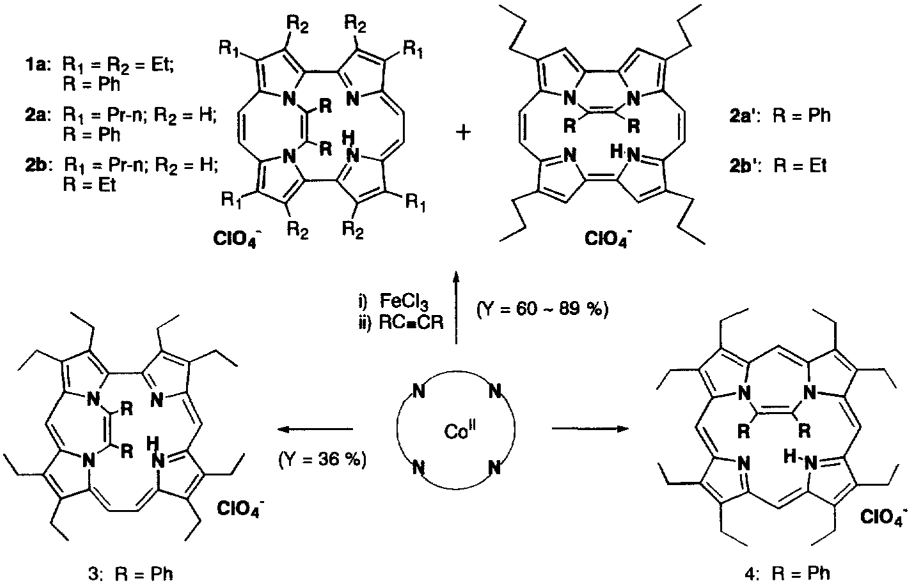
Abstract : N,N'-etheno-bridged porphycenes have been synthesized in good yields by the reaction of Co(II) porphycenes with acetylenes in the presence of $FeCl_3$. The etheno-bridge was introduced predominantly between the adjacent two nitrogens in the dipyrrylethene side rather than the dipyrrole side. These porphycenes are reduced at potentials more positive by ca. 0.5 V than those of the corresponding N,N'-etheno-bridged porphyrin analogues. © 1997 Elsevier Science Ltd.

Photochemistry and redox chemistry of porphyrins and related dye compounds have attracted considerable interests in view of the light-driven energy transfer and electron transfer processes mediated by chlorophylls in the photosynthetic system.[1] There have been many studies aimed at creating new dye compounds with superb photochemical and electrochemical properties based on the porphyrin molecular framework.[2,3] We have recently demonstrated that monocationic N(21),N(22)-bridged porphyrins show two reversible redox waves at potentials much more accessible ($E_{1/2}(P^+/P\bullet) = -0.72$ V and $E_{1/2}(P\bullet/P^-) = -1.22$ V)[4] than ordinary free base porphyrins.[5] We have already found that photo-induced single electron transfer (SET) occurs from N-benzyl-1,4-dihydronicotinamide (BNAH) to the monocationic N(21),N(22)-bridged porphyrins by visible light irradiation.[4] Since porphycene, a porphyrin isomer, is reduced at more positive potentials and more strongly luminescent than porphyrin,[6,7] the photochemical and electrochemical properties of the corresponding N,N'-bridged porphycenes are of considerable interest. In this paper are described the synthesis of N,N'-bridged compounds of the porphyrin isomers (porphycene and corrphycene) and their electrochemical properties in comparison with the porphyrin analogues.

We have shown that cobalt porphyrins react with acetylenes in the presence of Fe(III) salts to give good yields of N(21),N(22)-etheno-bridged porphyrins.[8] This reaction is closely related to the formation of N,N'-phenylene-bridged heme by the suicidal inactivation of cytochrome P450 with N-aminobenzotriazole which is known as a benzyne precursor.[9] The reaction proceeds by way of Co(III) porphyrin π-cation radicals and Co,N-etheno-bridged organometallic intermediates,[8] and is regarded as a versatile synthetic method for the N(21),N(22)-etheno-bridged porphyrins.[10]

When a blue dichloromethane solution (35 ml) of Co(II) octaethylporphycene, (OEPc)Co(II), (134 mg) was treated with $FeCl_3$ (5 equiv.), the visible absorption bands at 598 nm disappeared indicating that a Co(III)

π-cation radical was formed.[7] Diphenyl acetylene (5 equiv.) was then added to this thin brown solution to cause immediate coloration to green. After the reaction mixture was stirred for 2 hr at room temperature, it was treated with 10 % aqueous $HClO_4$ and then purified by silica gel chromatography to give a 67 % yield of N,N'-(PhC=CPh)(OEPc)$HClO_4$ (**1a**)[11]. The ^1H NMR signals due to the four methine protons of the porphycene periphery appear as two 2H-singlets at δ 10.00 and 9.76. This provides a strong evidence in support of the structure in which diphenyl acetylene bridges two nitrogens of the 1,2-dipyrrylethene unit but not of the dipyrrole unit. Although Co(II) 2,7,12,17-tetrapropylporphycene, (TPrPc)Co(II), similarly reacted with diphenyl acetylene in the presence of $FeCl_3$, the product turned out to be a mixture of two isomeric N,N'-bridged porphycenes in a ratio of 10 : 1 (89 % total yield). Since the chromatographic separation of these two isomers was unsuccessful, only the major isomer (**2a**)[12] could be isolated by repeated recrystallization. This isomer has the bridge on the 1,2-dipyrrylethene unit, while the minor isomer (**2a'**)[12] has the bridge on the dipyrrole unit. The latter showed two 2H-singlets due to the β-pyrrole protons at δ 9.31 and 8.80 and a pair of AB doublets associated to the peripheral vinylene protons at δ 9.57 and 9.17. Since signals due to the meta- and ortho-phenyl protons of the bridge moiety appear as a 4H-triplet and a 4H-doublet in the case of **2a**, the phenyl groups rotate fast on the NMR time scale. In contrast, the meta-phenyl protons of **2a'** are split into two broad 2H-signals appearing at higher magnetic fields (δ 5.60 and 4.58) than the corresponding protons in **2a** (δ 6.02). This indicates that the bridge moiety of **2a'** is closer to the porphycene plane and thus the free rotation of the phenyl group is restricted in comparison with **2a**. Chang and coworkers have recently reported the preparation of N,N'-methano-bridged tetrapropylporphycenes through the reaction of TPrPc free base with Vilsmeier reagents.[13] It should be noted that the one-carbon bridge was introduced exclusively into the 1,2-dipyrrylethene unit in their case.



As our organometallic reaction to synthesize N,N'-etheno-bridged porphyrins has now turned out to work well for porphycenes, we then went on to other porphyrin isomers, octaethylcorrphycene (OECc) and octaethylhemiporphycene (OEHPc). Although (OEHPc)Co(II) did not work at all, (OECc)Co(II) gave a 36% yield of N,N'-(PhC=CPh)(OECc)$HClO_4$ (**3**)[14] after purification on silica gel. A pair of AB doublets (δ 10.04 and 9.94) due to the peripheral vinylene protons in the ^1H-NMR spectrum are consistent with the structure in which two nitrogens on a dipyrrylmethene side are bridged by diphenyl acetylene to form a 7-membered ring. There was no indication of the formation of isomers with a 6-membered ring on a dipyrrole side or a 8-membered ring on a dipyrrylethene side.

Table 1. Half-wave redox potentials.[a]

Compd.	$E_{1/2}(P^+/P\bullet)$	$E_{1/2}(P\bullet/P^-)$	literature
1a	-0.16	(-0.56)[b]	this work
2a	-0.23	-0.61	this work
2b	-0.25	-0.63	this work
3	(-0.58)[b]	(-1.17)[b]	this work
4	-0.72	-1.22	ref. 4
$(OEPc)H_2$	-0.97[c]	-1.29[c]	ref. 6
$(TPrPc)H_2$	-0.93[c]	-1.30[c]	ref. 6
$(OEP)H_2$	-1.49[c]	-1.83[c]	ref. 5

[a] V vs. Ag/AgCl. [b] cathodic peak potential.
[c] The values were converted from the SCE standard in the literature to the Ag/AgCl standard here.

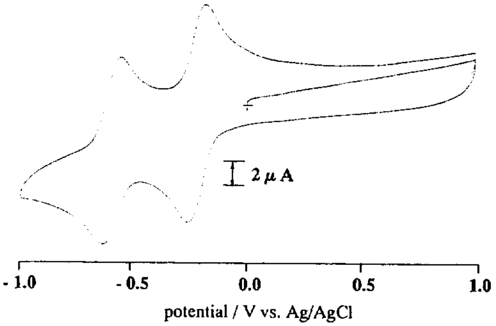


Figure 1. Cyclic voltammogram of **2a** in MeCN

Figure 1 shows a cyclic voltammogram of **2a** measured in acetonitrile using glassy carbon as a working electrode and a Ag/AgCl couple as a reference electrode using $(n\text{-}Bu)_4NClO_4$ (0.1 M) as an electrolyte. Two reversible waves observed for **2a** would correspond to the two one-electron reduction steps from a monocation to a radical, $E_{1/2}(P^+/P\bullet)$, and then to an anion, $E_{1/2}(P\bullet/P^-)$. It is worthy to note that the N,N'-bridged compounds are reduced at by 0.7 ~ 0.8 V more positive potentials than the parent free bases (see Table 1).[4-7] Furthermore, the half-wave potential is shifted by 0.56 V upon going from the octaethylporphyrin (OEP) isomer, N,N'-(PhC=CPh)(OEP)$HClO_4$ (**4**)[8], to the OEPc isomer **1a**.[6] This positive shift parallels the difference (0.52 V) in the reduction potentials between the parent free bases. Only a slight difference in the half-wave potentials was observed between the diphenyletheno bridge **2a** and the diethyletheno bridge (**2b**). It is remarkable that the OEPc derivative **1a** is reduced at a more positive potential than the TPrPc derivative **2a** in spite of the more electron-donating substituent effect in the former.[6] This probably points to the importance of the steric constraints between the peripheral substituents, because these steric constraints would distort the π-electron system out of the planar structure to lead to the significant changes in the electrochemical properties.

In conclusion, N,N'-etheno-bridged porphycenes were readily prepared by a one-step procedure as well as the porphyrin analogues. They are of great interest as redox couples in view of their reversibility and large positive shift in potential.

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11. (**1a**): ^{1}H NMR (δ, $CDCl_3$) 10.00, 9.76 (sx2, 2Hx2, -CH=); 3.8 ~ 3.4 (m, 16H, CH_2); 1.70, 1.42, 1.15, 0.95 (tx4, 6Hx4, CH_3); 3.44 (d, 4H, Phenyl-o-H); 6.12 (t, 4H, phenyl-m-H); 6.41 (t, 2H, phenyl-p-H); 4.51 (s, 1H, NH). UV-vis (λ_{max}(log ε) in CH_2Cl_2) 387 (4.89), 405 (sh, 4.67), 605 (4.35), 680 (4.41) nm. Anal. Calcd for $C_{50}H_{55}N_4O_4Cl$•(1/2)H_2O•(1/2)CH_2Cl_2: C, 70.28; H, 6.66; N, 6.49. Found: C, 69.94; H, 6.50; N, 6.59.
12. (**2a**): ^{1}H NMR (δ, $CDCl_3$) 10.35, 9.99 (sx2, 2Hx2, -CH=); 9.02, 8.92 (sx2, 2Hx2, pyrrole-β-H); 3.88, 3.72 (mx2, 4Hx2, CH_2Et); 2.28, 2.05 (mx2, 4Hx2, CH_2Me); 1.21, 1.01 (tx2, 6Hx2, CH_3); 3.67 (d, 4H, Phenyl-o-H); 6.02 (t, 4H, phenyl-m-H); 6.35 (t, 2H, phenyl-p-H); 4.28 (s, 1H, NH). UV-vis (λ_{max}(log ε) in CH_2Cl_2) 387 (4.97), 403 (sh, 4.85), 580 (4.22), 610 (4.32), 640 (4.53) nm. Anal. Calcd for $C_{46}H_{47}N_4O_4Cl$•(1/2)H_2O: C, 72.27; H, 6.33; N, 7.33. Found: C, 72.19; H, 6.13; N, 7.23. (**2a'**): ^{1}H NMR (δ, $CDCl_3$) 9.57, 9.17 (dx2, 2Hx2, -CH=, J = 11.5 Hz); 9.31, 8.80 (sx2, 2Hx2, pyrrole-β-H); 5.60, 4.58 (brx2, 2Hx2, phenyl-m-H); 6.21 (t, 2H, phenyl-p-H) (other signals are not detected because of the overlapping with strong signals due to the major isomer) .
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14. (**3**): ^{1}H NMR (δ, $CDCl_3$) 11.21, 10.38 (sx2, 1Hx2, -CH=); 10.04, 9.94 (dx2, 1Hx2, -CH=); 4.5 ~ 3.4 (m, 16H, CH_2); 2.00, 1.78, 1.76, 1.76, 1.71, 1.41, 1.39, 0.93 (tx8, 3Hx8, CH_3); 2.61, 2.45 (brx2, 2Hx2, Phenyl-o-H); 5.78, 5.76 (tx2, 2Hx2, phenyl-m-H); 6.16 (t, 2H, phenyl-p-H); -2.03 (br, 1H, NH). UV-vis (λ_{max}(log ε) in CH_2Cl_2) 427 (4.94), 586 (sh, 3.98), 614 (4.18) nm. Anal. Calcd for $C_{50}H_{55}N_4O_4Cl$•$2H_2O$: C, 70.86; H, 7.02; N, 6.61. Found: C, 70.97; H, 6.55; N, 6.66.

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