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SYNTHESIS OF FERROCENOPORPHYRINOPHANES STACKED WITH METALS AND AROMATIC RINGS

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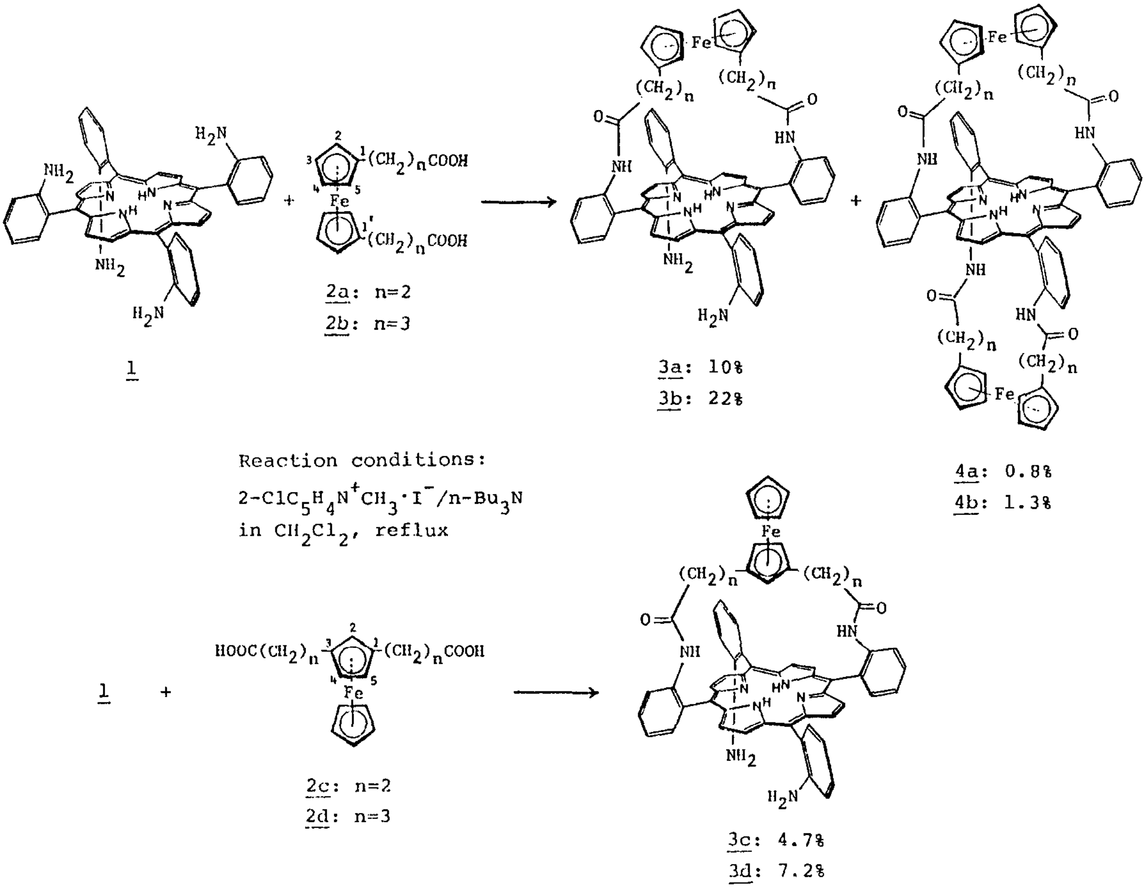
Summary: Double and triple layered porphyrinophanes bridged with 1,1'- or 1,3-disubstituted ferrocene moieties and their iron complexes have been synthesized.

Multi-layered porphyrins stacked with metal complexes are not only available as synthetic model systems of some hemoproteins,[1] but also for study on seeking novel conducting molecular metals.[2] We wish to report synthesis of (1,1')- and (1,3)ferrocenoporphyrinophanes which have double or triple layered structures consisting of ferrocene and tetraphenylporphyrin moieties.

Condensation of amines with acyl chlorides is generally used to form bridges of porphyrinophanes, but the reaction is not advantageous for the preparation of ferrocenoporphyrinophanes because of instability of ferrocenylacyl chlorides. Therefore, "Mukaiyama's method"[3] which provides a mild condition for amide or peptide synthesis was applied to the present work. Solutions of ferrocenedialkanoic acids (2),[4,5] αβαβ-tetrakis(o-aminophenyl)-porphyrin (1)[6] (1/2 in mole ratio = 1), 2-chloro-1-methylpyridinium iodide (2.4 mole equiv.) and tri-n-butylamine (4.8 mole equiv.) in freshly-distilled dichloromethane under conditions of high dilution ($\simeq 10^{-3}$ mol/l) were refluxed for 18 hr under an N_2 atmosphere. The reaction mixtures were worked up with saturated aq. Na_2CO_3, and the desired porphyrinophanes were isolated by repeated column and thin-layered chromatographies over silica gel from the crude containing many products. The typical results are shown in the scheme. Treatment of monobridged phane (3b) with acid (2b) under the same conditions as the above reaction gave dibridged phane (4b) in 10% yield. Dibridged phanes with 1,3-ferrocenedialkanoic acids (2c, 2d) have not yet isolated. It seems that the "Mukaiyama's procedure" is widely applicable to synthesis of porphyrinophanes linked with amide bridges if acid chloride is unstable or cannot be prepared.

The FD-mass and NMR spectral data of the products are summarized in



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2a: n=2
2b: n=3

3a: 10%
3b: 22%

4a: 0.8%
4b: 1.3%

Reaction conditions:
$2\text{-}ClC_5H_4N^+CH_3 \cdot I^- / n\text{-}Bu_3N$
in CH_2Cl_2, reflux

2c: n=2
2d: n=3

3c: 4.7%
3d: 7.2%

Table 1. In the ^{1}H-NMR spectra of monobridged (1,1')ferrocenoporphyrinophanes (3a, 3b), the pyrrole proton signals appear as a set of AB system and the cyclopentadienyl (Cp) ring proton signals are dramatically shifted to upfield in comparison with those of ferrocenedialkanoic acids (ca. δ4.0). Those spectral patterns indicate that the compounds (3a, 3b) have C_{2v} symmetry structures in which ferrocene moiety is layered over the porphyrin ring plane. The pyrrole protons of both 4a and 4b resonate as only one singlet signal. Appearance of the simplified signals reveals their D_{2d} symmetry features. The resonance fields of the Cp ring protons in the phanes (3a, 4a) bridged with propanoyl units are higher than those with butanoyl ones (3b, 4b). This observation is in accord with expectation based on a consideration with a CPK molecular model; the ferrocene moieties of the former are near to the porphyrin ring plane compared with the latter.

In (1,3)ferrocenoporphyrinophanes, the Cp ring proton signals at 2-position of 3c and 4,5-positions of 3d appear at the extremely high fields (δ0.20 and -0.02), whereas the 4,5-protons of 3c and the 2-proton of 3d (δ2.90 and 2.46) resonate in the vicinity of the unsubstituted Cp ring proton signals.

Table 1. FD-mass and NMR spectral data of ferrocenoporphyrinophanes

Compd.	FD-MS[a]	^{1}H-NMR[b], δ			^{13}C-NMR[c], δ	
	m/z	$-CH_2-$[d]	Cp-ring[d]	pyrrole	$-CH_2-$	Cp-ring
3a	969, $[M+1]^+$	0.80(4H,m)	1.33(4H,m)	8.70&8.88	23.83	65.83
		1.55(4H,m)	1.64(4H,m)	(each 4H,d)	38.55	66.86
						84.64
3b	996, M^+	0.45(4H,m)	1.68(4H,m)	8.76&8.88	25.48	66.28
		1.10(4H,m)	1.94(4H,m)	(each 4H,d)	27.24	66.87
		1.55(4H,m)			37.22	86.01
4a	1263, $[M+1]^+$	0.90(4H,m)	1.53(4H,m)	8.76(8H,s)	23.93	66.03
		1.55(4H,m)	1.81(4H,m)		38.40	67.00
						84.84
4b	1319, $[M+1]^+$	0.50(4H,m)	1.80(4H,m)	8.80(8H,s)	23.77	66.52
		1.10(4H,m)	2.17(4H,m)		27.47	66.93
		1.55(4H,m)			37.39	86.24
3c	968, M^+	0.55(4H,m)	0.20(1H,t)	8.75&8.90	24.60	65.17
		1.25(4H,m)	2.90(2H,d)	(each 2H,d)	38.98	66.75
			3.35(5H,s)	8.78&8.96		68.46
				(each 2H,d)		85.30
3d	997, $[M+1]^+$	0.27(4H,m)	-0.02(2H,d)	8.75&8.89	24.42	63.70
		1.18(8H,m)	2.46(1H,t)	(each 2H,d)	26.83	66.46
			2.82(5H,s)	8.81&8.96	36.40	68.28
				(each 2H,d)		85.19

[a] Only base peak is shown. [b] At 100MHz in $CDCl_3$. [c] At 25.2MHz in $CDCl_3$. [d] The signal assignments were determined by decoupling technique

Table 2. FD-mass and electronic absorption spectral data of ferroceno-porphyrinophane Fe(III)-Cl complexes and formation of Fe(II) complexes.

Phane	Fe(III)-Cl complex		Fe(II) complex		
	FD-MS[a] m/z	Absorption bands[b] nm	Reduction agent[c]	Base	Absorption band[b,d]
3a	1023, $[M+1-Cl]^+$	418,513,586,654,682	aa[e]	1-MeIm[f]	533
3b	1051, $[M+1-Cl]^+$	418,512,582,654,682	aa	1-MeIm	536
4a	1317, $[M+1-Cl]^+$	421,513,580,652,685	aa	NH_3	534
4b	1373, $[M+1-Cl]^+$	422,513,582,656,681	aa	1-MeIm	535
3c	1023, $[M+1-Cl]^+$	420,515,583,655,683	$NaBH_4$	1-MeIm	543
3d	1086, $[M+1]^+$	418,510,580,652,680	$NaBH_4$	1-MeIm	537

[a] Only base peak is shown. [b] In CH_2Cl_2. [c] In CH_2Cl_2/H_2O at r.t. [d] Only characteristic band is shown. [e] Ascorbic acid. [f] 1-Methylimidazole.

These spectral behaviors mean that the ferrocene nuclei of the phanes are greatly inclined to the porphyrin ring plane, and that the directions of the inclination in 3c and 3d are reversed each other. The interesting difference of the conformations may arise from the lengths of the bridging chains and the resultant steric requirement, but is still not elucidated without uncertainty.

Metallation of the phanes with $FeCl_2$ in DMF/pyridine by refluxing for 10 min afforded the corresponding Fe(III)-Cl complexes in satisfactory yields (60-95%). The complexes were characterized by means of FD-mass and electronic absorption spectra (Table 2). The distances between the two irons in 3a- and 3b-Fe(III) are ≈6 and ≈7Å, and those between the iron of the porphyrin and the centre of the nearer Cp ring in 3c- and 3d-Fe(III) are ≈5 and ≈6Å, respectively, in consideration with a CPK molecular model. Fe(III) of all complexes were converted to Fe(II) by reduction with ascorbic acid or $NaBH_4$ in CH_2Cl_2/H_2O under the presence of 1-methylimidazole except for 4a-Fe(III) complex, which could be reduced under the presence of ammonia (Table 2). Treatments of the Fe(II) complexes with dioxygen in CH_2Cl_2 at -60°C gave absorption spectra that suggested formation of O_2-complexes. The detailed results will be published elsewhere.

The iron complexes here synthesized would be available as a synthetic model system for the reactions of cytochrome C with ferrocene and its derivatives[7] or electrochemical redox reaction of cytochrome C on the electrode derivatized with a [2]ferrocenophane.[8]

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