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A NEW ROUTE TO PORPHYRINS SUBSTITUTED WITH LONG ALKOXY GROUPS, ATTEMPTS TO PREPARE THE DISCOTIC LIQUID CRYSTALS

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Abstract. Pyrroles substituted with long alkoxy groups are prepared by the reaction of iminodiacetic acid dimethyl ester and dimethyl oxalate and the subsequent alkylation. These pyrroles are good precursor molecules for the corresponding porphyrins, which are expected to form an ordered columnar mesophase and are able to co-ordinate to various metals.

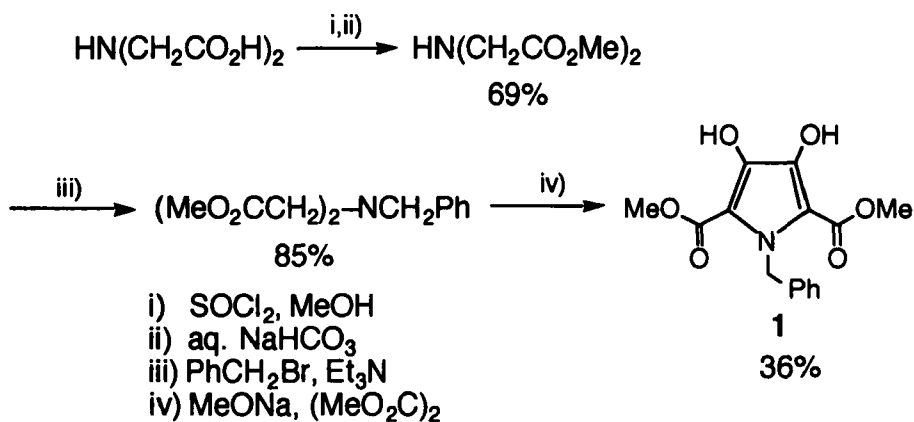
INTRODUCTION

Porphyrins are of exceeding importance in photodynamic therapy (PDT)¹ and of particular interest as conducting materials, nonlinear optics or liquid crystals. Meso-5,10,15,20-tetraarylporphyrins² and 2,3,7,8,12,13,17,18-octaalkylporphyrins³ are readily accessible. However, symmetric-octaalkoxy porphyrins, except the simplest octamethoxy porphyrin,⁴ are not reported because of the lack of good general method to obtain pyrroles substituted with long alkoxy groups.

We report a new synthesis of porphyrins and their metal complexes substituted with long alkoxy groups.

SYNTHESIS OF PORPHYRINS SUBSTITUTED WITH LONG ALKOXY GROUPS

Chemical modification of pyrroles at 3- and 4- positions can control electrical properties of the corresponding porphyrins. According to this conception, we investigated and reported the general synthetic route of 3,4-disubstituted pyrroles based on the condensation of nitroalkenes and ethyl isocyanoacetate.⁵ This method consisted of Michael addition, however, it was not applicable to the synthesis of pyrroles with electron-donating groups such as hydroxy and alkoxy groups. Therefore, dihydroxypyrrole **1** was prepared according to the literature procedure (Scheme 1).⁴

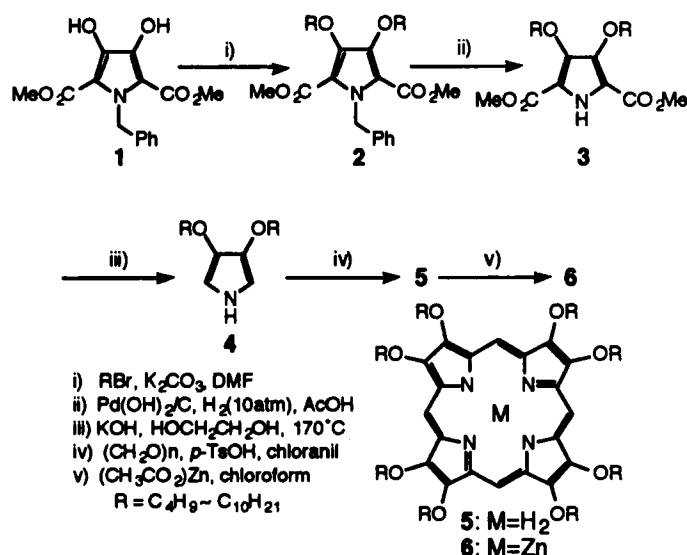


SCHEME 1 Synthesis of 3,4-dihydroxy pyrrole

Thus, methylation of iminodiacetic acid followed by treatment with benzyl bromide in the presence of triethylamine gave a N-benzyl-iminodiacetic acid dimethyl ester which was then treated with dimethyl oxalate, giving a N-benzyl-3,4-dihydroxy pyrrole **1** in moderate yield.

Alkylation of **1** was carried out with haloalkanes in the presence of potassium carbonate. When dry acetone was used as a solvent, this alkylation was quite unsatisfactory to give pyrrole **2** in low yield. But the yields of these pyrroles **2** were improved by the use of dry N,N-dimethyl formamide as a solvent (Scheme 2, Table 1). The debenzoylation of these pyrroles **2** were performed at 50 °C in the presence of Pd(OH)₂/C and hydrogen at a pressure of 10 atm. The ester function of **3** could be readily removed by heating at 170 °C with KOH in ethylene glycol to afford α-free pyrroles **4** in good yields, which were precursors for symmetrical porphyrins substituted with long alkoxy groups **5**. Porphyrins **5** were obtained by the reaction of **4** with paraformaldehyde under acid catalysis, followed by oxidation with *p*-chloranil.

Free base porphyrins **5** could be purified by repeated silica gel and alumina column chromatography, but this isolation method was considerably troublesome and the yields were very low. Therefore, those porphyrins were isolated after complexation. Thus, the reaction mixture was evaporated under vacuo and the residue was subsequently converted to Zn-complex by treatment with zinc diacetate in chloroform.



SCHEME 2 Porphyrins substituted with long alkoxy groups

The yields of each step were listed in Table 1.

TABLE 1 Yields of pyrroles and porphyrins prepared

	R	Yield/%			
		2	3	4	6
a	n-C ₄ H ₉	89	72	99	17
b	n-C ₆ H ₁₂	94	87	93	11
c	n-C ₈ H ₁₇	93	78	99	43
d	n-C ₁₀ H ₂₁	95	90	91	9

APPROACH TO LIQUID CRYSTALS

In recent years, it has become apparent some of compounds such as porphyrin octaesters, octakis(β -octoxyethyl)porphyrin and octa(dodecyl)tetrapyrzinoporphyrine exhibit columnar mesophase⁶. These new discotic liquid crystals bear the long alkyl chains and disk-like structure as common structural characteristics.

The alkoxy porphyrins prepared have also long alkoxy groups and disk-like center core. Therefore, these compounds may show a liquid crystalline phase. The detailed characters were under investigation.

EXPERIMENTAL

A typical procedure is exemplified by the preparation of 2,3,7,8,12,13,17,18-octahexyloxyporphyrin Zn complex **6b**.

N-Benzyl-2,5-dicarboxymethyl-3,4-dihexyloxy pyrrole 2b

N-Benzyl-2,5-dicarboxymethyl-3,4-dihydroxy pyrrole **1** (3.1g, 10 mmol) was stirred with potassium carbonate (6.9g, 50 mmol) and 1-bromohexane (4.91 ml, 30 mmol)

in dry DMF (8 ml) at 50 °C for 24 h. The mixture was extracted with ethyl acetate and the extract was washed with water and evaporated. Chromatography of the residue gave the title compound **2b** as a yellow oil in 94 % yield. ^1H NMR (CDCl_3) δ 0.91 (6H, t, J 6.01), 1.30-1.46 (12H, m), 1.69-1.79 (4H, m), 3.80 (6H, s), 4.03 (4H, t, J 6.56), 5.99 (2H, s) and 6.90-7.25 (5H, m); ^{13}C NMR (CDCl_3) δ 14.0, 22.6, 25.6, 30.0, 31.6, 48.7, 51.5, 75.1, 116.5, 125.8, 126.7, 128.3, 139.0, 142.7 and 160.7; $\nu_{\text{max}}/\text{cm}^{-1}$ 3100-2800, 1720 and 1600-1100; m/z (EI) 473 (M^+ , 100) 357 (65) and 273 (74).

2,5-Dicarboxymethyl-3,4-dihexyloxy pyrrole **3b**

Paradium catalyst ($\text{Pd}(\text{OH})_2/\text{C}$, 0.89g) was placed in a hydrogenation bottle and suspended by the addition of 16 ml of glacial acetic acid, then the system was flushed several times with hydrogen. A solution of N-benzyl-2,5-dicarboxymethyl-3,4-dihexyloxy pyrrole **2b** (1.77g, 5 mmol) in glacial acetic acid (7 ml) was added to a stirred suspension with a slow stream of hydrogen. With the initial reading on the pressure gauge about 10 atm, the bottle was heated at 50 °C for 48 h. The catalyst was removed by filtration through a celite pad and washed with methanol. The filtrate was evaporated under vacuo and the residue chromatographed to yield the title compound **3b** as a yellow oil in 87 % yield. ^1H NMR (CDCl_3) δ 0.90 (6H, t, J 6.71), 1.25-1.48 (12H, m), 1.69-1.76 (4H, m), 3.90 (6H, s), 4.09 (4H, t, J 6.41) and 8.90 (1H, brs); ^{13}C NMR (CDCl_3) δ 13.7, 22.4, 25.3, 39.7, 31.3, 51.5, 74.7, 113.2, 141.5 and 160.1; $\nu_{\text{max}}/\text{cm}^{-1}$ 3452, 3000-2800, 1722 and 1292; m/z (EI) 383 (M^+ , 15), 229 (15), 215 (94), 183 (100) and 151 (16).

3,4-Dihexyloxy pyrrole **4b**

To a solution of 2,5-dicarboxymethyl-3,4-dihexyloxy pyrrole **3b** (1.15g, 3 mmol) in ethylene glycol (15 ml) was added potassium hydroxide (0.50g, 9 mmol). After being boiled under reflux for 4h under an argon atmosphere the mixture was extracted with chloroform, washed with water and evaporated. Silica gel chromatography of the residue gave the title compound **4b** as a colorless solid in 93 % yield. All operations were performed under an atmosphere of argon. m.p. 55.0-55.5 °C, ^1H NMR (CDCl_3) δ 0.89

(6H, t, J 6.56), 1.26-1.48 (12H, m), 1.70-1.81 (4H, m), 3.86 (4H, t, J 6.72), 6.19 (2H, d, J 3.05) and 7.00 (1H, brs); ^{13}C NMR (CDCl_3) δ 14.0, 22.6, 25.7, 29.4, 31.6, 71.6, 100.7 and 137.5; $\nu_{\text{max}}/\text{cm}^{-1}$ 3480, 3056, 300-2800, 1500-1240 and 800-700; m/z (EI) 263 (M^+ , 93), 183 (26), 99 (100), 98 (26) and 100 (25).

2,3,7,8,12,13,17,18-Octahexyloxyporphyrin 5b

Into a solution of 3,4-dihexyloxy pyrrole **4b** (0.267g, 1 mmol) and paraformaldehyde (0.036g, 1.2 mmol) in dry toluene (20 ml), argon was slowly bubbled through from needle for 15 min. *p*-Toluenesulfonic acid (0.0038g, 0.02 mmol) was added to a mixture and stirred at 55 °C for 15 h in the dark. After the reaction mixture was cooled to ambient temperature, *p*-chloranil (0.147g, 0.6 mmol) was added to the mixture which was then stirred at ambient temperature for 24 h. The mixture was washed with aqueous sodium hydroxide and water, dried and evaporated. The residue chromatographed repeatedly to obtain a trace amount of the title compound **5b**. ^1H NMR (CDCl_3) δ -4.4 (2H, s), 0.90-1.90 (72H, m), 2.22-2.29 (16H, m), 4.97 (16H, t, J 6.35) and 10.1 (4H, s); ^{13}C NMR (CDCl_3) δ 14.1, 22.8, 26.1, 30.6, 31.9, 75.8, 94.4, 96.1 and 143.3; m/z (EI) 1111(M^+ , 5), 150(90) and 104(100); UV/nm λ_{max} 381, 498, 534, 563 and 617.

2,3,7,8,12,13,17,18-Octahexyloxyporphyrin Zn complex 6b

The residue obtained above was dissolved in chloroform without any purification, to which was added zinc diacetate and stirred for 4 h at room temperature. The mixture was washed with water, dried and evaporated. The residue was purified by silica gel chromatography to give the title compound **6b** as a red solid. ^1H NMR (CDCl_3) δ 0.98-1.01 (24H, m), 1.46-1.60 (32H, m), 1.85-1.91 (16H, m), 2.25-2.30 (16H, m), 4.98 (16H, t, J 6.59) and 10.12 (4H, s); ^{13}C NMR (CDCl_3) δ 14.2, 22.8, 26.1, 30.7, 31.9, 75.8, 95.2, 140.9 and 114.2; m/z (EI) 1175 (M^+ , 14), 1174 (26) and 1173(34); UV/nm λ_{max} 396, 530, 562 and 571.

Structural proof of other compounds **2-4a,c,d** and **6a,c,d** were accomplished through ^1H NMR, ^{13}C NMR and MS spectrum.

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