SYNTHSIS AND SPECTRAL PROPERTIES OF BIS- AND TRIS(METALLOPORPHYRINS)

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In order to obtain the titled compounds, various mono- and difunctional porphyrins were prepared as follows. According to the Johnson's stepwise porphyrin synthesis, 2-(2-ethoxycarbonylethyl)-3,7,8,13,17,18-hexamethyl-12-propylporphin (1) and 2-(2-ethoxycarbonylaminoethyl)-3,7,8,17,18-hexamethyl-12-ethylporphin (2) were synthesized in 34% and 41% yields, respectively. 1 was hydrolyzed in hydrochloric acid to give the corresponding carboxylic acid porphyrin (3). The LiAlH$_4$ reduction of 1 was carried out in THF to afford 2-(3-hydroxypropyl)-3,7,8,17,18-hexamethyl-12-propylporphin (4). When a solution of 2 in 2—ethoxyethyl alcohol was refluxed in the presence of potassium hydroxide, pure 2-(2-aminoethyl)-3,7,8,13,17,18-hexamethyl-12-propylporphin (5) was obtained on cooling. Mesoporphyrin-IX dimethyl ester (6) was converted into a mixture of two isomers of the monomethyl ester (7) on partial hydrolysis, while the LiAlH$_4$ reduction gave 3,7-bis(3-hydroxypropyl)-2,8,13,18-tetramethyl-12,17-diethylporphin (8).

3 was converted into the acyl chloride (9) with use of thionyl chloride, followed by the treatment with 5 in the presence of triethylamine, and the bisporphyrin (10) linked by amide bonding was obtained in a 28% yield. When the acyl chloride (11) of 7 was treated with 4 in dichloromethane in the presence of triethylamine, the bisporphyrin (12) linked by ester group was obtained in a 55% yield. A highly diluted solution of the diacyl chloride of 6 was combined with a solution of 8, and the double-bridged bisporphyrin (13) was isolated in a 28% yield. Single-bridged trisporphyrin (14) was synthesized by treatment of two molar amount of the acyl chloride (9) with 8 in a 50% yield. The multiporphyrins (10, 12, 13, and 14) were all converted into the Zn, Cu, and Mg complexes.

The visible spectra of the Zn and Cu complexes of the multiporphyrins are no longer superposed on that of the metal complexes of 6, indicating the strong interaction between the macrocycles due to the dimer formation. While the fluorescence of the Zn complexes of multiporphyrins suffers intramolecular self-quenching considerably, the Mg complexes exhibit only slight decrease in the fluorescence intensity caused by the intramolecular self-quenching.