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The synthesis and characterisation of a C₆ hydrocarbon linked porphyrin dimer and its zinc complex is described. From fluorescence quantum yields and excited singlet and triplet state lifetimes, recorded for the dimers and the corresponding monomer species, it is suggested that the dimeric porphyrins exist in solution in open and closed conformations. The open conformations retain photophysical properties similar to those of the relevant monomeric species but the closed conformations do not fluoresce.

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Introduction.

There is considerable interest in the design and characterisation of porphyrin dimers and higher order aggregates because of their involvement in photosynthesis [1], catalysis [2], photoconduction [3] and phototherapy [4]. A large number of different types of covalently-linked porphyrin dimers has been reported [5-15]. Both flexible and relatively rigid linkages have been employed but, in many cases, the linkage is suspect to breakage under operating

conditions. In this paper, we describe the synthesis of a porphyrin dimer possessing a stable C₆ hydrocarbon linkage. Related compounds have been prepared previously [13] using a different synthetic approach and possessing different substituents in the porphyrin ring.

Because of the wide interest shown in the photochemical properties of porphyrin aggregates [16-22], we have measured the excited state lifetimes of the dimeric species. The triplet excited state is found to be long-lived but there

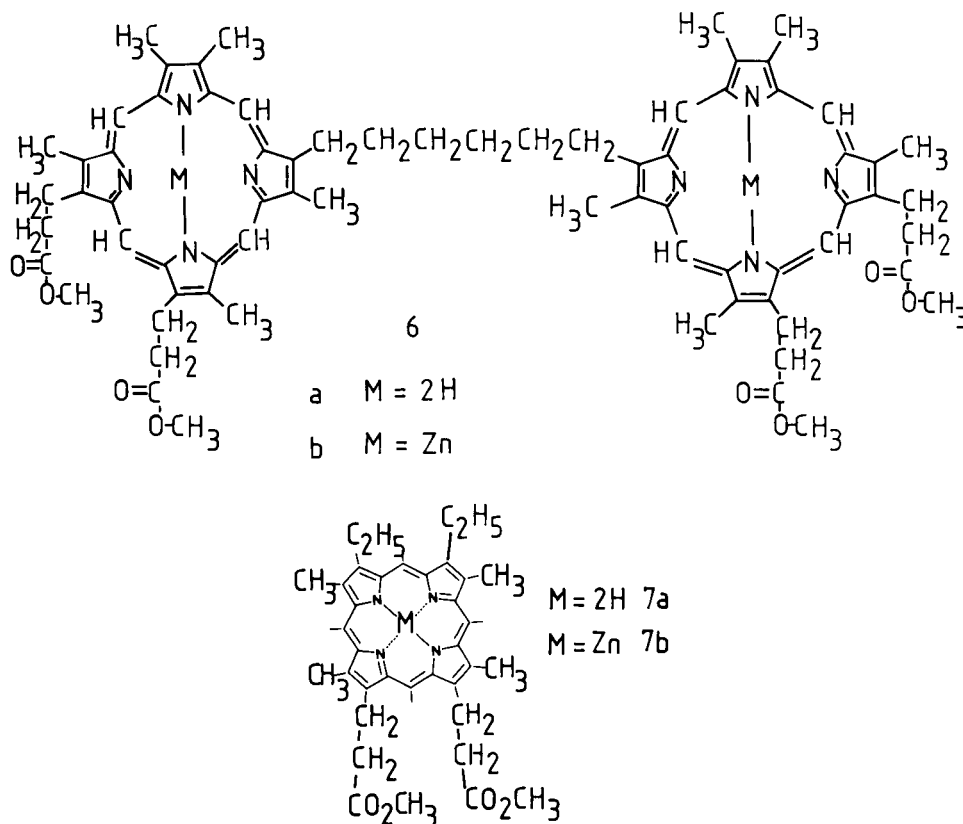


Figure 1. Structures of the free-base and zinc porphyrin monomers and dimers used in this study.

appears to be some exciton coupling in the singlet excited state manifold, especially in benzene solution. The flexible nature of the connecting linkage allows a large number of conformations to be adopted [19,20] and this complicates interpretation of the data.

Results and Discussion.

The structures of the dimers are given by Figure 1. A hydrocarbon linkage between the two porphyrin rings was selected because it should be much more robust than the amide or ester linkages normally employed in such systems. The six membered carbon chain ensures a high level of rotational degrees of freedom so that a large number of closely related conformations can be adopted in solution. The two porphyrin rings can approach each other quite closely or, in the other extreme, they can be separated by about 3 nm. Since there is little barrier to rotation around the C-C bonds, conformational exchange could be relatively fast [23]. Each porphyrin ring is substituted with two propionic acid moieties since this structure closely resembles natural porphyrins and the pyrrole rings were substituted only with methyl groups so that the nmr pattern of the bridging methylene protons could be resolved and assigned.

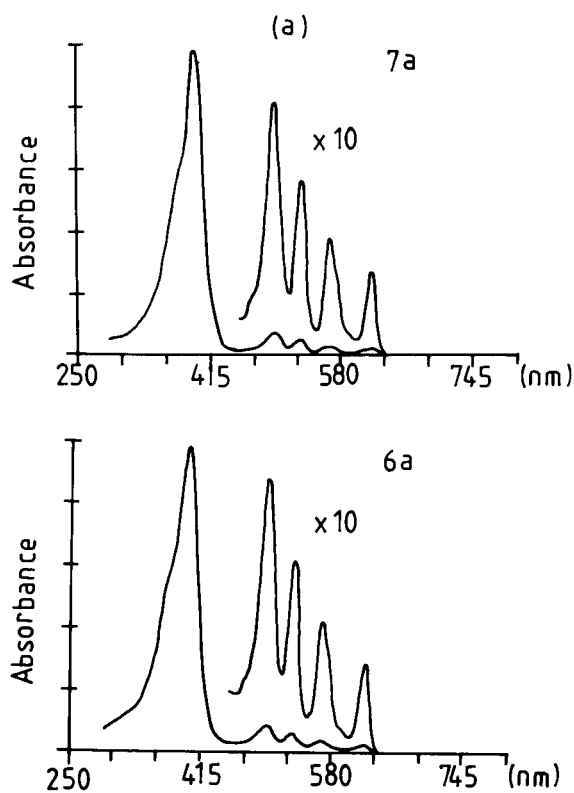


Figure 2. (a) Absorption spectra of the monomeric and dimeric free-base porphyrins **7a** and **6a** respectively in dilute dichloromethane solution.

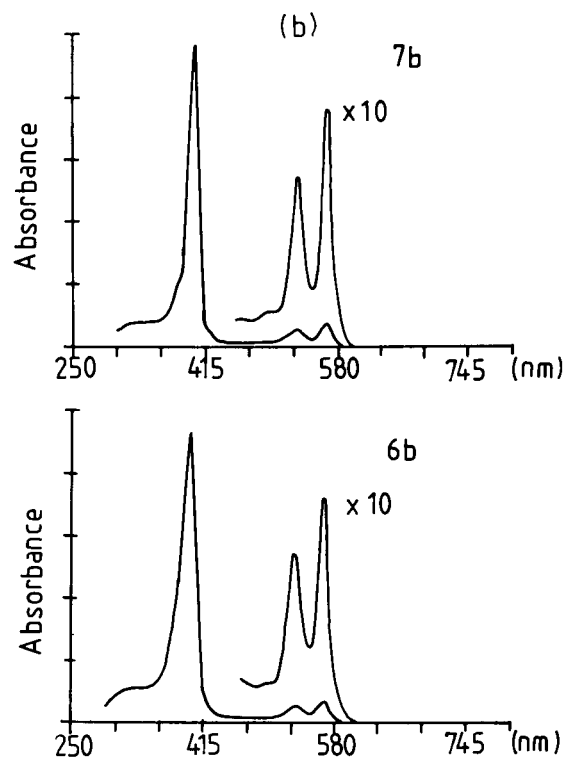


Figure 2. (b) Absorption spectra of the monomeric and dimeric zinc porphyrins **7b** and **6b** respectively in dilute dichloromethane solution.

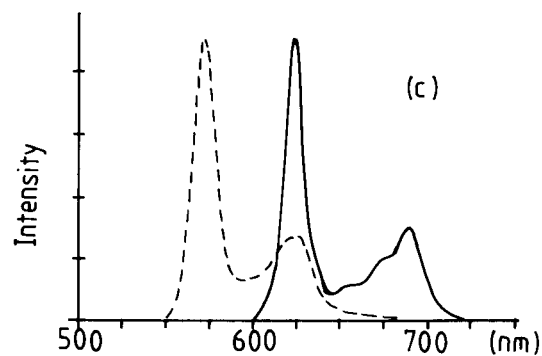


Figure 2. (c) Fluorescence spectra of the monomer porphyrins **7a** (—) and **7b** (---) in dilute dichloromethane solution.

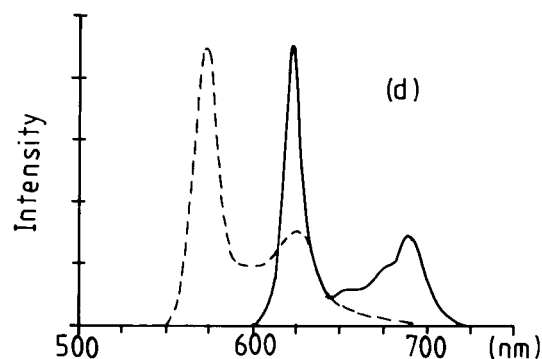


Figure 2. (d) Fluorescence spectra of the dimeric porphyrins **6a** (—) and **6b** (---) in dilute dichloromethane solution.

The covalently-bonded porphyrin dimer **6a** was found to be poorly soluble in organic solvents and insoluble in water. Modest solubility was found in dichloromethane and benzene. The nmr spectra recorded for **6a** confirmed the presence of the bridging C₆ chain but mass spectra recorded with electron impact ionisation exhibited only monomeric porphyrin fragmentation patterns. The use of a FAB-mass spectrometer facilitated observation of the dimeric porphyrin ions and the fragmentation pattern of the propionic acid sidechain involved a McLafferty rearrangement.

Insertion of zinc ions into the porphyrin rings of the dimer **6a** was accomplished by standard methods [24]. The resulting dizinc complex **6b** was found to be even less soluble than the corresponding free-base porphyrin dimer. Solutions of **6b** in benzene were stable upon storage over several days but photodecomposition occurred in chlorinated solvents. Also, it was found that solid samples of **6b** decomposed upon storage in air over a few days. Such stability problems were not observed with the free-base dimer **6a** and all spectroscopic studies reported for **6b** were made with freshly prepared material.

Absorption and fluorescence spectra recorded in dilute dichloromethane solution for the two porphyrin dimers **6a** and **6b** and the corresponding monomer species **7a** and **7b** are collected in Figure 2. The absorption spectra show the normal features expected [25] for porphyrins, namely an intense Soret or B-band centered around 400 nm and either two or four less-intense Q-bands stretching across the visible region. Comparison of the relevant monomer and dimer species shows that, in both cases, the Soret band of the dimer is slightly broadened and blue-shifted. The Q-bands are essentially unaffected by the covalent linkage. The zinc complex shows slightly more perturbation, with a 200 cm⁻¹ blue-shift in the Soret band upon forming the dimer. These absorption spectral changes can be ascribed to exciton coupling interactions between the two porphyrin rings in the dimers [21,26]. In benzene solution, the extent of exciton coupling is greater.

Fluorescence spectra of monomer and dimer species are almost identical. Fluorescence quantum yields (ϕ_f) and excited singlet state lifetimes (τ_s) were measured for each compound in air-equilibrated solution and the results are collected in the Table. Fluorescence from the zinc complexes is much less intense than from the corresponding free-base porphyrins and the singlet state lifetimes are much shorter due to the internal heavy-atom effect [27].

For each system in dichloromethane solution, the fluorescence yields and singlet state lifetimes of each monomer/dimer couple are comparable (*i.e.* $\pm 10\%$). However, in dilute benzene solution this is not the case. Here, the measured fluorescence quantum yields show that fluorescence from each dimer is much less efficient

Table
Photophysical Properties of the Various Porphyrins in Dilute Solution

Porphyrin	Solvent	ϕ_f	τ_s (ns)	τ_s (μ s)
7a	dichlorobenzene	0.095	10.7	470
	benzene	0.107	12.7	240
6a	dichlorobenzene	0.094	10.6	250
	benzene	0.057	11.9	200
7b	dichlorobenzene	0.043	1.4	85
	benzene	0.051	1.6	63
6b	dichlorobenzene	0.037	1.5	210
	benzene	0.028	1.5	32

than from the corresponding monomer. For the two systems, fluorescence from the dimer is only 54% as efficient as that from the monomer (Table). The excited singlet state lifetimes are more comparable and the dimers give values only about 10% quenched relative to the monomers.

These results can be rationalised in terms of the various conformations that can be adopted by the dimeric porphyrins in solution [21]. In dichloromethane solution the two porphyrin head groups in the dimers appear to be almost ignorant of each others existence. In benzene solution, about 40% or so of each dimer exists in a ground state conformation in which the two porphyrin rings are held in a special arrangement (probably in very close proximity). Excitation of this conformation results in formation of species which show little fluorescence and possess short (*i.e.* < 0.2 ns) singlet state lifetimes. The other 60% or so of the dimer molecules exist in benzene solution in conformations which retain fluorescence yields and lifetimes similar to those associated with the relevant monomeric porphyrins. Probably, these are open conformations with the two porphyrin rings held well apart. For this simple picture to be a reasonable representation of the real situation it is necessary that rotational relaxation of the porphyrin rings in the dimers is slow compared to the excited singlet state lifetimes. The poor solubility of the dimers in benzene solution prevents a detailed analysis of the average conformations adopted by these compounds.

The above situation requires that the open conformations in both benzene and dichloromethane solutions are frozen for times shorter than 10 ns. The maximum centre-to-centre separation distance possible in the dimers is about 3 nm and accepting [28] that the porphyrin ring has a diffusion coefficient of about 2×10^{-6} cm² s⁻¹ the translational distance that can be achieved in 10 ns is approximately 2.0 nm. Thus, there may be some barrier to free movement of the porphyrin rings and there is growing evidence that this is the case [6,19-21].

The Table also contains the triplet excited state lifetimes (τ) measured in dilute, outgassed solution. Most-ly, the dimeric porphyrins exhibit somewhat shorter triplet state lifetimes than found for the corresponding monomers. The value determined for **6b** in dichloromethane solution does not fit into the general trend but, as mentioned in the experimental section, this compound undergoes facile photodecomposition in halogenated solvents and the derived τ values may be erroneous. Omitting this value, the triplet lifetimes observed for the dimeric porphyrins are at least 50% of the value observed for the corresponding monomeric porphyrin. This suggests that, even though the triplet states are relatively long-lived, exciton coupling within the triplet manifold is weak.

EXPERIMENTAL

Melting points were determined on a Kofler Boetius apparatus. Absorption spectra were recorded in dichloromethane (porphyrins) or 1% hydrogen bromide in chloroform (tripyrrenes and biladienes) solution using either a Hitachi ESP-3T or a Perkin-Elmer 554 spectrophotometer. Infrared spectra were recorded with a Perkin-Elmer 257 instrument and nmr spectra were obtained with Bruker WM250 and WHFT400 machines using tetramethylsilane as internal reference. Mass spectra were recorded with a Varian MAT-731 (ionisation *via* electron impact) and an AEI MS902 (direct insertion) spectrometers. Analytical grade tlc was performed on Kavalier Silufol and Merck Kieselgel 60 F₂₅₆ plastic sheets and preparative scale tlc and column chromatography was made with Kavalier Silica LS-40 using chloroform/acetone 5/1.

Fluorescence spectra were recorded in dilute solution using a Perkin-Elmer MPF4 spectrofluorimeter. All spectra were fully corrected for spectral responses of the instrument [29]. Fluorescence quantum yields were determined by the optically dilute method using octaethylporphyrin as standard. Singlet excited state lifetimes were measured by time-correlated single photon counting [21]. Triplet excited state lifetimes were measured by conventional flash photolysis using outgassed solutions. An Applied Photophysics 200J instrument was used with the flash lamps filtered to remove light of wavelength < 500 nm. The fluorescence quantum yield measurements had a reproducibility of $\pm 5\%$ whilst the excited state lifetime values are accurate to within 5% of the quoted value.

3,3'-bis(2,4-Dimethyl-1-ethoxycarbonylpyrrolyl)-1,6-dioxohexane-1,6 (2).

A mixture of stannic chloride (11.6 ml) and adipinic dichloroanhydride (6.4 ml) was added dropwise to a suspension of 2,4-dimethyl-5-ethoxycarbonylpyrrole (**1**) (15 g) in dry dichloroethane (25 ml) cooled to 0°. After 45 minutes, the liquid was decanted and the solid material was poured into cold water (200 ml) acidified to pH 2 with hydrochloric acid. The precipitate was filtered, washed with water and twice recrystallised from *N,N*-dimethylformamide, yield 17.1 g (86%), mp 263-264°, R_f 0.61; ir (potassium bromide): ν max 3280, 1650 cm^{-1} ; ^1H nmr (deuteriochloroform): δ 8.91 (s, NH), 4.41 (s, CH_2CH_3), 3.22 (t, COCH_2), 3.13 (s, CH_3), 2.89 (s, CH_3), 1.53 (t, CH_2CH_3), 1.42 (m, CH_2CH_2); ms: m/e (240°) 444 (M^+ , 88%), 399 (8), 383 (5), 277 (36), 222 (16), 208 (100), 198 (21), 191 (7), 177 (6), 167 (30).

Anal. Calcd. for $\text{C}_{24}\text{H}_{32}\text{N}_2\text{O}_6$: C, 64.84; H, 7.26; N, 6.30. Found: C, 64.68; H, 7.41; N, 6.50.

3,3'-bis(2,4-Dimethyl-5-ethoxycarbonylpyrrolyl)hexane-1,6 (3a).

The above bispyrrole **2** (15 g) was suspended in anhydrous tetrahydrofuran (250 ml) containing sodium borohydride (5.48 g) under nitrogen. Boron trifluoride etherate (26.2 g) was added dropwise to the well-stirred suspension kept at 0° and the mixture was then stirred at room temperature for one hour. The solution was poured into water (500 ml) and the precipitate was filtered, washed with warm water and recrystallised from

N,N-dimethylformamide, yield 11.2 g (80%), mp 189-190°, R_f 0.79; ir: ν max 3310, 1700 cm^{-1} ; ^1H nmr (deuteriochloroform): δ 8.55 (s, NH), 4.25 (c, CH_2CH_3), 2.25 (t, 1,6- CH_2), 2.17 (s, CH_3), 2.09 (s, CH_3), 1.30 (m, CH_2CH_3 and 2,5- CH_2), 1.24 (m, 3,4- CH_2); ms: m/e 416 (M^+ , 76%), 371 (56), 363 (8), 343 (10), 326 (14), 296 (11), 266 (13), 208 (31), 194 (18), 180 (100), 135 (72).

Anal. Calcd. for $\text{C}_{24}\text{H}_{36}\text{N}_2\text{O}_4$: C, 69.20; H, 8.71; N, 6.73. Found: C, 68.98; H, 8.64; N, 6.65.

3,3'-bis(2,4-Dimethylpyrrolyl)hexane-1,6 (3b).

A suspension of the bispyrrole **3a** (1.25 g) in a mixture of ethanol (25 ml) and water (8 ml) containing sodium hydroxide (1.7 g) was heated to boiling for six hours. The ethanol was removed under vacuum and the residue was dissolved in water (30 ml) containing sodium hydroxide (3 g) and a few drops of hydrazine hydrate. The solution was then heated at 160-165° in a stainless steel autoclave for five hours. After cooling to room temperature, the compound was extracted with chloroform (3 x 100 ml). The solvent was dried with sodium sulfate and removed under vacuum and the residue chromatographed on a silica column using chloroform as eluent to give pale green crystals, yield 0.51 g (62%), mp 118-120°, R_f 0.9; ir: ν max 3360 cm^{-1} ; ^1H nmr (deuteriochloroform): δ 7.55 (s, NH), 6.34 (c, 5,5'-H), 2.22 (t, CH_2), 2.03 (c, CH_3), 1.87 (c, CH_3), 1.46 (m, 2,5- CH_2), 1.20 (m, 3,4- CH_2); ms: m/e 272 (M^+ , 100%), 257 (16), 178 (10), 164 (8), 150 (6), 136 (7), 122 (28), 108 (83), 94 (13).

3,3'-bis(2,4-Dimethyl-5-formylpyrrolyl)hexane-1,6 (3c).

The above bispyrrole **3b** (0.51 g) was stirred in *N,N*-dimethylformamide (10 ml) at 0° and treated with phosphoryl chloride (0.9 ml) in *N,N*-dimethylformamide (2 ml) to form the Vilsmyer complex. After stirring for two hours at room temperature, saturated aqueous sodium carbonate solution (70 ml) was added and the mixture was stirred vigorously at 60° for two hours. Water (150 ml cm^3) was added and the bispyrrole was extracted with chloroform (3 x 100 ml cm^3). The combined extracts were dried with sodium sulfate and evaporated to dryness under reduced pressure. The residue was chromatographed on a silica column using chloroform/acetone 5/1 as eluent, yield 408 mg (66%), mp 224-226°, R_f 0.35; ir: ν max 3240, 1760 cm^{-1} ; ^1H nmr (deuteriochloroform): δ 9.52 (s, CHO), 8.73 (s, NH), 2.18 (t, 1,6- CH_2), 2.07 (s, CH_3), 1.85 (s, CH_3), 1.42 (m, 2,5- CH_2), 1.18 (m, 3,4- CH_2); ms: m/e 328 (M^+ , 28%), 299 (12), 270 (23), 206 (7), 136 (34), 122 (17), 107 (100), 93 (6).

Anal. Calcd. for $\text{C}_{20}\text{H}_{28}\text{N}_2\text{O}_2$: C, 73.13; H, 8.59; N, 8.53. Found: C, 72.98; H, 8.46; N, 8.57.

2,2'-bis(1,3,7,13,17,18-Hexamethyl-8,12-(2-methoxycarbonyl)ethyl)-10,24-dihydro-21*H*-bilinato)hexane-1,6-tetrabromohydrate (5).

A solution of hydrogen bromide (40%) in acetic acid (0.65 ml) was added to a suspension of the tripyrrene **4** [30] (338 mg) and the bispyrrole **3c** (104 mg) in acetic acid (0.6 ml) and methanol (4 ml). The mixture was heated at 60° for 10 minutes and, after cooling, diethyl ether (25 ml) was added dropwise to precipitate the bisdibiladiene (**5**) as fine pink crystals, yield 445 mg (92%), mp > 330°; λ max 451, 519 nm.

Anal. Calcd. for $\text{C}_{72}\text{H}_{94}\text{Br}_4\text{N}_8\text{O}_8$: C, 56.92; H, 6.24; N, 7.38; Br, 21.04. Found: C, 57.09; H, 6.36; N, 7.37; Br, 20.65.

2,2'-bis(3,7,8,12,18-Pentamethyl-13,17-(2-methoxycarbonyl)ethyl)porphyrinato)hexane-1,6 (6a).

A solution of the above bisdibiladiene **5** (80 mg) in 1,2-dichlorobenzene (200 ml) containing iodine (135 mg) was heated to boiling for 20 minutes. After cooling to room temperature, triethylamine (0.4 ml) was added and the solution was filtered through a column of alumina. The porphyrin layer was washed with petroleum ether and eluted with chloroform. The porphyrin was rechromatographed on silica and recrystallised from pyridine/acetic acid to give purple crystals, yield 24 mg (38%), mp > 350°, R_f 0.65; λ max (dichloromethane): 395, 495, 528, 564, 618 nm; δ ^1H nmr (deuteriochloroform): 10.94, 10.58, 10.54, 10.40 (4s, meso-H), 4.50 (m, $\text{CH}_2\text{CH}_2\text{CO}_2$), 4.03 (t, 1,6- CH_2), 3.59 (m, 7CH_3), 3.16 (m, $\text{CH}_2\text{CH}_2\text{CO}_2$), 1.93 (m, 2,5- CH_2), 1.49 (m, 3,4- CH_2); ms: m/e (fab) 1070 (3%), 1069 (8), 1068 (14), 1018 (8), 1017 (3), 988 (4), 987 (12), 986 (14), 926

(6), 925 (12), 924 (18), 923 (6), 616 (23), 615 (38), 592 (36), 591 (62), 579 (46), 578 (76), 503 (66), 502 (100).

Anal. Calcd. for C₁₂H₈N₈O₈: C, 72.82; H, 6.96. Found: C, 73.06; H, 6.87.

Dizinc Complex of the Bisporphyrin **6b**.

The above bisporphyrin **6a** (8 mg) was dissolved in chloroform (15 ml) and a few ml of a saturated solution of zinc acetate in methanol was added. The mixture was refluxed for 10 minutes and then poured into water (150 ml). The organic layer was separated, dried with sodium sulfate and evaporated to low volume. The red porphyrin solution was chromatographed on silica using chloroform as eluent, yield 8.4 mg (96%), mp > 350°, R_f 0.6; λ max (dichloromethane): 397, 529, 565 nm.

Anal. Calcd. for C₂₂H₁₈N₈O₈Zn₂: C, 65.80; H, 5.98; N, 8.53. Found: C, 65.71; H, 5.88; N, 8.55.

Mesoporphyrin III Dimethyl Ester (7).

This compound **7a** was synthesized and purified by the procedure reported before [30]; λ max (dichloromethane): 397, 498, 530, 566, 620.

Zinc was inserted into the porphyrin ring as above to give the corresponding zinc complex **7b**; λ max (dichloromethane): 400, 530, 566 nm.

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