Symmetrically Tetra-substituted Phthalocyanines

Nagao Kobayashi,*[a] Yoshiyuki Nishiyama,[a] Toshie Ohya,[b] and Mitsuo Sato[b]

[a] *Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Katahira, Sendai 980, Japan*
[b] *Biophysics Division, Faculty of Pharmaceutical Sciences, Teikyo University, Sagamiko, Kanagawa 199–01, Japan*

Symmetrically tetra-substituted phthalocyanines with four quinone or porphyrin units attached have been synthesised and some of their spectroscopic properties are reported.

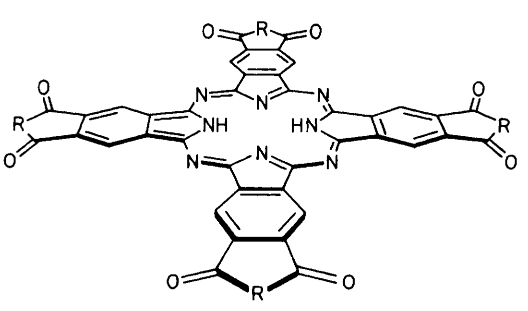
There are many types of tetra-substituted porphyrin. For example, phenyl, anthracenyl,[1] furyl,[2] crownyl,[3] ferrocenyl,[4] porphyrinyl,[5] and even carbaboranyl groups[6] (the last example retains a pocket capable of binding small molecules) have been employed as substituents. Various tetra-substituted phthalocyanines have also been prepared.[7] However, unlike the porphyrin examples, all the previously reported tetra-substituted phthalocyanines were mixtures of four positional isomers. In view of this, we propose the use of the tetra-anhydride of 2,3,9,10,16,17,23,24-octacarboxyphthalocyanine (OCPc) (**1**), as a convenient precursor for the preparation of symmetrically tetra-substituted phthalocyanines. In order to demonstrate the utility of (**1**), we report here the synthesis, identification, and some spectroscopic properties of the four quinone unit-attached phthalocyanines (**2**) and (**3**) and the tetraporphyrinylphthalocyanines (**5a**) and (**5b**). The former are novel non-metallated phthalocyanines which show no fluorescence owing to efficient intramolecular quenching.[8] The latter are not only the first examples of mixed porphyrin–phthalocyanine multimers but represent also a first step toward metal complex-substituted phthalocyanines.

Compound (**1**) was obtained in 90% yield by refluxing

OCPc[9] in benzene–acetyl chloride (1 : 1 v/v).† Compound (**1**) was then treated with a slight excess of 1- or 2-aminoanthraquinone in *N*-methyl-2-pyrrolidone at 70 °C for 5 h under nitrogen and the solution was diluted with benzene after cooling. The precipitate was heated *in vacuo* at 200 °C for 12 h, then redissolved in the minimum amount of dimethylformamide (DMF), and benzene added to reprecipitate the product. This procedure was repeated three times, and (**2**) and (**3**) were obtained in 38 and 77% yields, respectively. The reference compound (**4**) was obtained similarly using decylamine in 61% yield.

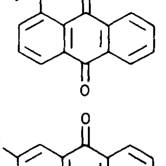
The ground-state absorption spectra (Figure 1A) of (**2**)—(**4**) are essentially identical and are not perturbed markedly by the presence of the attached anthraquinone molecules.‡ However, we were unable to detect fluorescence emission from degassed dimethyl sulphoxide (DMSO)–benzene (1 : 4 v/v) solutions except for (**4**) over the range 550—900 nm. In order to clarify the nature of the interaction between the phthalocyanine and anthraquinone moieties in (**2**) and (**3**), the interaction between (**4**) and anthraquinone was examined. When (**4**) (7.89×10^{-7} M) was irradiated in the presence of anthraquinone in DMSO–benzene (1 : 4 v/v), quenching of the fluorescence was observed which depended on the concentration of anthraquinone. By extending the anthraquinone concentration–fluorescence intensity relationship for (**4**) to the zero fluorescence intensity of (**2**) and (**3**), the 'effective concentration' of one anthraquinone molecule in (**2**) and (**3**) to quench the fluorescence of (**4**) intramolecularly was estimated to be at least 2.0×10^{-3} M. Thus, this datum suggests very extensive intramolecular quenching in (**2**) and (**3**), although the anthraquinone units in these compounds are not necessarily located in close proximity to the phthalocyanine plane.

As in the preparation of (**2**)—(**4**), (**5a**) was obtained from (**1**) and 5-(*p*-aminophenyl)-10,15,20-triphenylporphyrin (**6**)[10] in 73% yield (recrystallized from CH_2Cl_2–MeOH). Although from its n.m.r. spectrum the integrated number of aromatic protons in (**5a**) (116) was proportional to the number (8) of pyrrole protons of the peripheral porphyrins, classical proof of structure (**5a**) was obtained by identification of the products of alkaline hydrolysis (25 M NaOH, 24 h in the dark). The molar ratios of (**6**) and OCPc were 4.00 : 0.96 (±0.03) as compared with the theoretical ratio 4.00 : 1.00, supporting the tetra-substituted structure of (**5a**). The absorption spectra of this multimer (Figure 1B) showed evidence of interaction of components (**1**) and (**6**). The Soret band was broadened (22 nm half-width, 70% increase in half-width) but its position was unchanged and its absorption coefficient (ε) was about 32% of [4 times the ε value of (**6**) at the Soret band + ε of (**1**) at 418 nm]. The decrease in Q band intensity was also significant [29% of that of (**1**) alone]. With respect to the band positions,

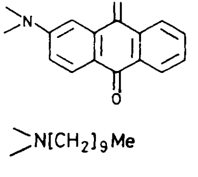


(**1**) R = —O—

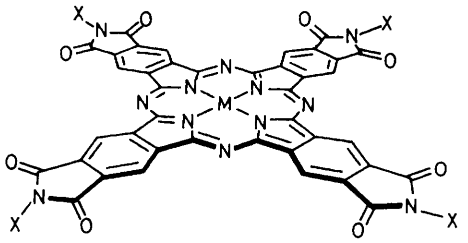
(**2**) R =

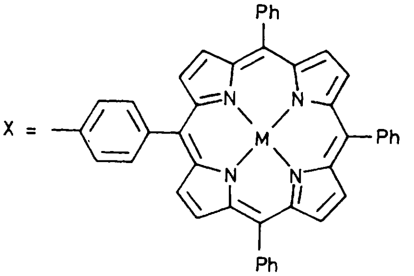


(**3**) R =



(**4**) R = $>N[CH_2]_9Me$





(**5a**) M = H_2
(**5b**) M = Fe
(**6**) = XNH_2, M = H_2

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† Satisfactory elemental analyses were obtained for (**1**)—(**5**). Spectroscopic data: (**1**), $\nu_{max.}$ (KBr) 1837 and 1772 cm^{-1}; $\lambda_{max.}$ (DMF–DMSO 9 : 1 v/v) 713 (ε 148 000), 687 (135 500), 653 (63 100), 625 (46 800), and 350 (85 400) nm; m.c.d. (DMF–DMSO 9 : 1 v/v) 331 ($[\theta]_M \times 10^{-4}$/deg dm^3 mol^{-1} cm^{-1} T^{-1} 5.26), 370(−6.26), 629(43.1), 641(40.1), 681(97.2), and 704(−192.4) nm. (**2**), $\nu_{max.}$ (KBr) 2920, 1770, 1710, and 1670 cm^{-1}; $\lambda_{max.}$ (DMSO–benzene 1 : 4 v/v) 644 nm (ε 13 300); m.c.d. (DMSO–benzene 1 : 4 v/v) 320 ($[\theta]_M \times 10^{-4}$ 0.21), 372(−0.32), 435(−0.49), 623(4.59), and 705(−3.74) nm. (**3**), $\nu_{max.}$ (KBr) 2925, 1770, 1710, and 1665 cm^{-1}; $\lambda_{max.}$ (DMSO–benzene 1 : 4 v/v) 648 nm (ε 13 500); m.c.d. (DMSO–benzene 1 : 4 v/v) 318 ($[\theta]_M \times 10^{-4}$ 0.32), 378(−0.65), 437(−0.49), 622(4.13), 678(−2.56), and 707(−3.28) nm. (**4**), $\nu_{max.}$(KBr) 2920, 1770, and 1710 cm^{-1}; $\lambda_{max.}$ (DMSO–benzene 1 : 4 v/v) 644 nm (ε 13 300); m.c.d. (DMSO–benzene 1 : 4 v/v) 318 ($[\theta]_M \times 10^{-4}$ 0.33), 373(−0.49), 432(−0.37), 628(4.60), 682(−2.77), and 704(−3.90) nm; ^1H n.m.r. δ($CDCl_3$) 7.3—6.2 (8H, br.s), 4.1—3.1 (8H, br.t), 2.1—0.6 (76H, m), −8.5 to −12.7 (2H, v br.s, peak at δ −10.6). (**5a**), $\nu_{max.}$(KBr) 2920, 1780, and 1715 cm^{-1}; $\lambda_{max.}$ (DMF) 418 (ε 412 000), 519 (29 000), 650 (35 500), and 693 (42 800) nm; m.c.d. (DMF) 415 ($[\theta]_M \times 10^{-4}$ 86.3), 425(−78.5), 625(15.1), 683(16.3), and 701(−30.6) nm; ^1H n.m.r. ([$^2H_7$]DMF) 7.50—8.95 (116H, m) and −2.92 (8H,s).

‡ It was reported that the effect of substituents on the absorption spectrum of phthalocyanine is small (P. G. Seybold and M. Gouterman, *J. Mol. Spec.*, 1969, **31**, 1). However, introduction of four imino groups into (**1**) to produce (**2**)—(**4**), caused dramatic changes in the absorption spectrum to give the spectrum in Figure 1A. Very intense reduction of absorption coefficients (hypochromism) was recognized especially in the Q-band region.

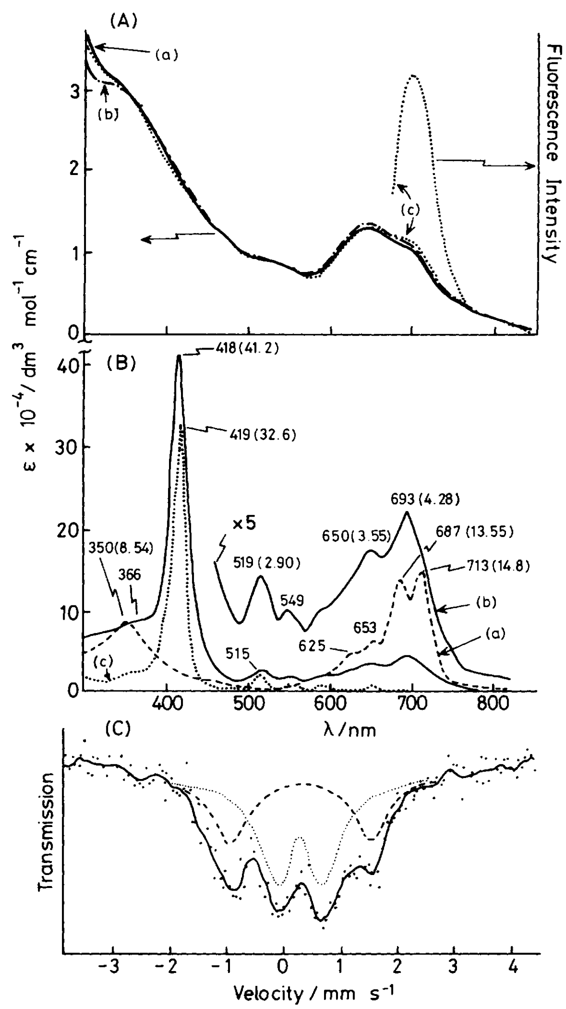

Figure 1. (A) Absorption and emission spectra of (a) (**2**), (b) (**3**), and (c) (**4**) in DMSO–benzene (1 : 4 v/v). Excitation was at 633 nm at room temperature. (B) Absorption spectra of (a) (**1**) in DMF–DMSO (9 : 1 v/v), (b) (**5a**) in DMF, and (c) (**6**) in DMF. (C) Mössbauer spectra of (**5b**) at 4.5 K. The velocity scale is relative to Fe metal. The solid line represents the average of the experimental data (dots) and the dotted and dashed lines are two doublets constructed so that their sum reproduce the solid lines.

those originating mainly from the porphyrin (**6**) did not shift, while those from the phthalocyanine (**1**) shifted significantly, *i.e.* the Soret band shifted to the red and the Q band to the blue by 1250 and 450 cm^{-1}, respectively.

Figure 1C shows the Mössbauer spectrum of (**5b**), the iron derivative of (**5a**).§ The spectrum could be fitted by a sum of two components by a least-squares approximation assuming Lorenzian line shapes; the ratio of the areas under inner and outer doublets was *ca.* 4 : 1, reflecting the structure (**5b**). Judged from the Mössbauer parameters, the isomer shift (δ) and quadrupole splitting (ΔE_Q),[11] the inner doublet (δ 0.37, ΔE_Q = 0.88 mm s^{-1}) corresponds to high-spin iron(III) (iron in porphyrin moiety) and the outer doublet (δ 0.44, ΔE_Q 2.57 mm s^{-1}) to intermediate-spin iron(II) (iron in phthalocyanine moiety). Thus, in (**5b**) iron exists in two oxidation states.¶

The use of (**1**) and its metal complexes thus has the following merits in the derivatization of phthalocyanines. (i) Any compounds including amino groups can be attached to (**1**) and its metal complexes in one step. (ii) The resultant compounds are symmetrical and isomers are not produced. (iii) The preparation of phthalonitrile and/or phthalic anhydride precursors is avoided.

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§ Compound (**5b**) was obtained by the reaction of (**5a**) and $FeCl_2$ in refluxing DMF under N_2 and subsequent treatment with dilute HCl.

¶ The δ and ΔE_Q values of iron-inserted (**4**) were 0.30 and 1.96 mm s^{-1} at 4.3 K, respectively (our unpublished data). On the other hand, those of *meso*-tetraphenylporphyrinatoiron(III) chloride were 0.52 and 1.51 mm s^{-1} at 4.2 K, respectively (J. P. Collman, J. L. Hoard, N. Kim, G. Lang, and C. A. Reed, *J. Am. Chem. Soc.*, 1975, **97**, 2676).

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