

A New Phthalocyanine Analogue Containing One 1,8-Naphthalene Unit

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Phthalocyanines (Pcs) are composed of four benzo-fused pyrroles, while hemiporphyrines are composed of two benzo-fused pyrroles and two pyridine molecules. Namely, central metals in these compounds are surrounded by four five-membered rings (Pc) and two five-membered and two six-membered rings (the latter). However, pc-like molecules with three five-membered rings and one six-membered ring are very rare, although such a molecule was once suggested in the literature.¹ In this communication, we report the first well-characterized such example, *i.e.* (7,12:14,19-diimino-5,32:21,30-dinitrilo-2,3,9,10,16,17-hexa-*n*-butoxy-21*H*,32*H*-tribenzo-*[c,h,m]*naphtho[4,5-*r,s*][1,6,11,16]tetraazacycloheneicosanato-(2-)-*N*³³,*N*³⁴,*N*³⁵,*N*³⁶)zinc(II), **1** (inset of Figure 1). As will be shown below, the electronic states of this compound are unusual and can be explained using a "five-orbital model".

Compound **1** was obtained by fusing 1,8-dicyanonaphthalene (2 mmol)² and 1,2-dibutoxy-4,5-dicyanobenzene (2 mmol)³ in the presence of zinc acetate (1.1 mmol) and hydroquinone (1 mmol) at 250–260 °C for *ca.* 20 min under nitrogen, followed by purification by basic alumina and gel-permeation (Bio-Beads SX8, Bio-Rad) chromatography and then recrystallization from dichloromethane–hexane in a 48% yield. FAB mass, elemental analysis, and ¹H NMR data were satisfactory.⁴

Figure 1 shows the electronic absorption, magnetic circular dichroism (MCD), and fluorescence emission and excitation spectra of **1** in tetrahydrofuran (THF). In the absorption spectrum, two peaks are seen above 700 nm, while the shape of the spectrum in the region 300–700 nm resembles that of ZnPcs.⁵ The MCD spectrum is similar in shape to that of ZnPcs at 300–700 nm, while a Faraday *B* term appears corresponding to the absorption peak at the longest wavelength. Fluorescence emission was observed from both the S₁ and S₂ excited states, and a mirror-image relationship was seen with the respective excitation spectra. However, no emission was detected from the states corresponding to the absorption peaks at 797 and 748 nm.⁶ The quantum yield (Φ_F) of the S₁ emission ($\Phi_F = 0.53$) was higher than that of ZnPc in 1-chloronaphthalene ($\Phi_F = 0.30$)⁷ but lower than that of the corresponding ZnPc with eight

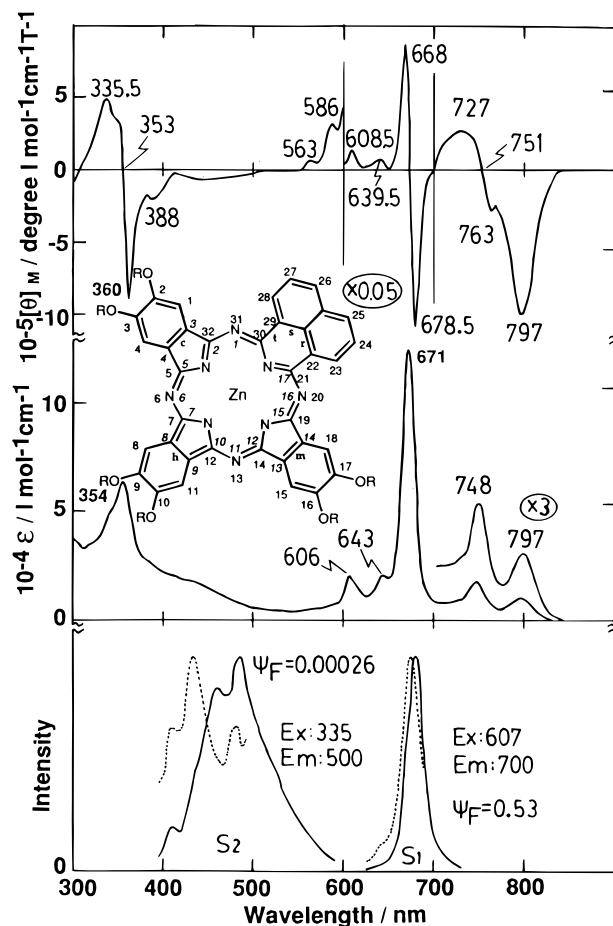


Figure 1. Electronic absorption (middle), MCD (top), and fluorescence emission and excitation (bottom) spectra of compound **1**. Excitation was at 607 and 335 nm for S₁ and S₂ emissions, respectively. There is no intensity relationship between the S₁ and S₂ emissions. Magnetic field = 1.2 T. The inset shows the structure and numbering system of compound **1**.

butoxy groups at the 1,4,8,11,15,18,21,25-positions in THF ($\Phi_F = 0.62$).⁸ The lifetime of the S₁ emission ($\tau = 4.07$ ns) was fairly similar to that of general ZnPcs, and the Φ_F value of the S₂ emission was 2.6×10^{-4} , which is also typical of the S₂ emission of Pcs.⁹

In order to obtain structural information, the structure of **1** was optimized using the MNDO method, which was implemented in the MOPAC93 MO Package,¹⁰ and the π -system of the structure shown in Figure 1 was drawn on the basis of the results. The starting structure was constructed using standard Pc X-ray structural data^{11a} and naphthalene.^{11b} Our attention was particularly focused on the stability of the bonds in the

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(4) *m/e*: 995 (M⁺ - Zn). Anal. Calcd for C₆₀H₆₆N₈O₈Zn: C, 67.94; H, 6.27; N, 10.56. Found: C, 67.52; H, 6.23; N, 10.37. ¹H NMR (500 MHz, CD₂Cl₂): δ 6.0–9.1 (br, 12H, arom), 3.92 (br s, 12H, OCH₂), 0.7–2.3 (br m, 42H, aliph). We were concerned about contamination by (1,4,8,11,15,18,21,25-octabutoxy)ZnPc, since a trace of this compound would have a great influence on the interpretation of the spectra. Accordingly, the utmost care was taken to remove this species.

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(6) However, with excitation at 745 nm, a very small emission, perhaps too weak to be called an S₁ emission, was detected at 802 nm. Such a phenomenon is observed for Pc analogues which show weak absorption bands in the near-IR region. For example, naphtho-fused Pc shows a similar phenomenon (our unpublished results).

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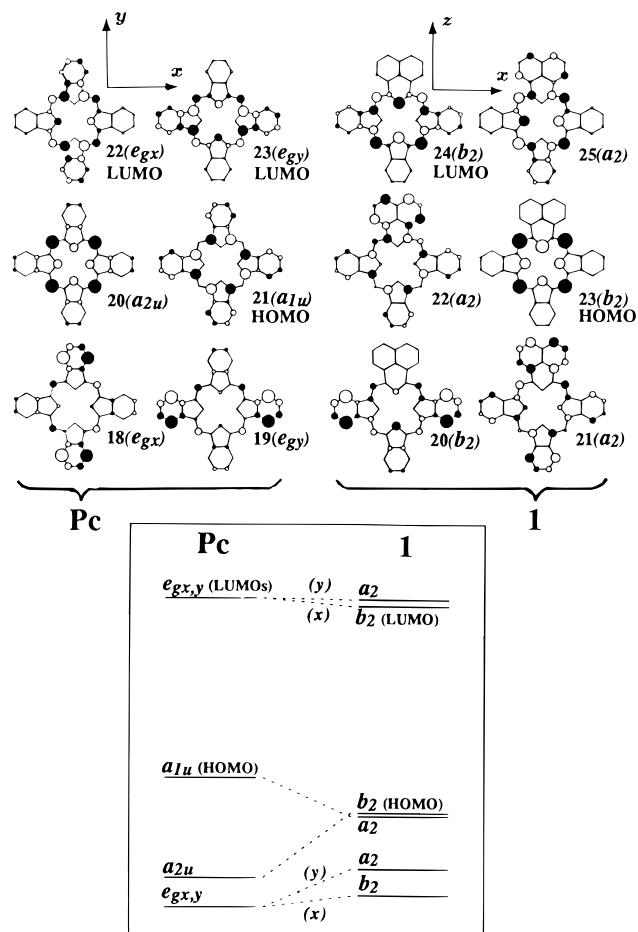


Figure 2. Some frontier MOs of the compound **1** dianion (top, right) and the Pc dianion (top, left) and correlation diagram between MOs of Pc and **1** (bottom). Note that the e_g orbitals have degenerate levels.

pyridine moiety. In the equilibrium structure, the distances between N of pyridine and adjacent carbons (C_2) and between carbons C_2 and C_3 are 1.388 and 1.493 Å, respectively. Since the corresponding lengths in pyridine are 1.330 and 1.373 Å,¹² it is concluded that bonding lengths in the pyridine ring in **1** are increased and therefore that bonds in this moiety may be weaker.

In order to aid the interpretation of the absorption spectrum, molecular orbital (MO) calculations were performed within the framework of the Pariser–Parr–Pople (PPP) approximation¹² for the dianion of **1**, and the results were compared with the values for the Pc dianion. The degenerate LUMOs of the Pc dianion (e_g orbitals) split into two orbitals in **1** due to the lowering of the molecular symmetry from D_{4h} to C_{2v} . It is well-known from group theory that the electronic transitions of highly symmetrical molecules obey severe selection rules. For example, only $e_g \leftarrow a_{1u}$ or $e_g \leftarrow a_{2u}$ transitions can be observed in the absorption spectra of metallo-Pcs with D_{4h} symmetry.⁵ When the symmetry is lowered substantially by chemical modification, some symmetrically forbidden transitions become allowed, thereby producing new absorption bands. For a C_{2v} molecule, as with **1**, there is no forbidden $\pi-\pi^*$ transition and only the polarizabilities of transitions are dominated by symmetry, as $a_2 \leftrightarrow b_2$ (x -polarized) and $a_2 \leftrightarrow a_2$ and $b_2 \leftrightarrow b_2$ (z -polarized).

Figure 2 (top) shows some frontier MOs of Pc and **1**, and Figure 2 (bottom) displays their correlation diagram. The most striking result was found in the order of the HOMOs; that is, with the introduction of the 1,8-naphthalene unit, the second HOMO of Pc (a_{2u}) is unstabilized by intense electron delocalization onto the eight nitrogen atoms, while the first HOMO of Pc (a_{1u}) is stabilized by electron delocalization onto the outer

(in particular onto the naphthalene) rings. Consequently, the order of the energy levels of these MOs is inverted, and the large energy gap between the HOMO and second HOMO of Pc becomes nearly zero or degenerate in **1**.

The degenerate MOs of Pc (e_g) are also influenced strongly by the substitution, since the degeneracy originates from the high (more than C_3) symmetry of the molecule. Hence, all the degenerate e_{gx} and e_{gy} pairs turn out to be nondegenerate b_2 and a_2 orbitals in C_{2v} symmetry, respectively. It is also observed that the y component of the degenerate third HOMOs of Pc (e_g) is unstabilized with the symmetry lowering. As a result, the third highest occupied level approaches the level of the nearly degenerate two HOMOs, and transitions from these three orbitals can mix through configuration interactions with the help of the new selection rules mentioned above.

Five calculated transition energies in the visible–near-IR region and their assignments are as follows together with the experimental values (the values are in the following order: energy in eV (nm), oscillator strength, configurations, polarizations of transitions, and the wavelengths of the corresponding bands observed in nm). Band 1: 1.780 (697), 0.02, $22 \rightarrow 24$ (57%), $23 \rightarrow 25$ (41%), x , 797. Band 2: 1.913 (648), 0.01, $23 \rightarrow 24$ (53%), $22 \rightarrow 25$ (42%), z , 748. Band 3: 2.782 (446), 2.34, $22 \rightarrow 25$ (52%), $23 \rightarrow 24$ (30%), $21 \rightarrow 25$ (8%), z , 679. Band 4: 2.875 (432), 0.98, $23 \rightarrow 25$ (43%), $22 \rightarrow 24$ (36%), $21 \rightarrow 24$ (13%), x , 668. Band 5: 3.281 (378), 1.13, $21 \rightarrow 24$ (74%), $23 \rightarrow 25$ (12%), x , 354. Although the calculated values are not necessarily in good agreement with the observed values, the order of band energies and intensities results in quite persuasive interpretations for the band assignments. As discussed above, the three HOMOs participate in the transitions to the two lowest vacant MOs in this energy region. This indicates that five orbitals should be taken into account to describe the electronic and spectroscopic properties of **1** (the estimated contribution of the third HOMO is 8–13% as mentioned above). In particular, it is of interest to be able to consider the reason for the appearance of a Faraday A -term-like curve corresponding to the absorption peak at 671 nm. From the calculated results, one could readily conclude that this band consists of two closely lying transitions with nearly degenerate levels, *i.e.* as a superimposition of two Faraday B terms.¹⁴ Since these transitions have mutually orthogonal x and z polarizations, the excited states behave just as the excited states of D_{4h} molecules, that is, like $E_{u,x}$ and $E_{u,y}$ forming a pseudo A term in MCD spectra.⁵ In addition, the energy diagram of **1** (Figure 2, bottom) suggests that the situation is somewhat similar to that of general metal-free porphyrins in that not only two HOMOs but also two LUMOs are severally nearly degenerate. This in turn suggests that two small peaks observed at 797 and 748 nm may correspond to the Q band while the intense peak at 671 nm may have a character similar to that of the Soret band of general metal-free porphyrins. Indeed, the intensity of the two bands at 748 and 797 nm is roughly 1 order of magnitude smaller than that at 671 nm, as observed commonly for the Q and Soret bands of metal-free porphyrins.

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