

Planar Phthalocyanine–Pyrazinoporphyrazine Heterodinucleates

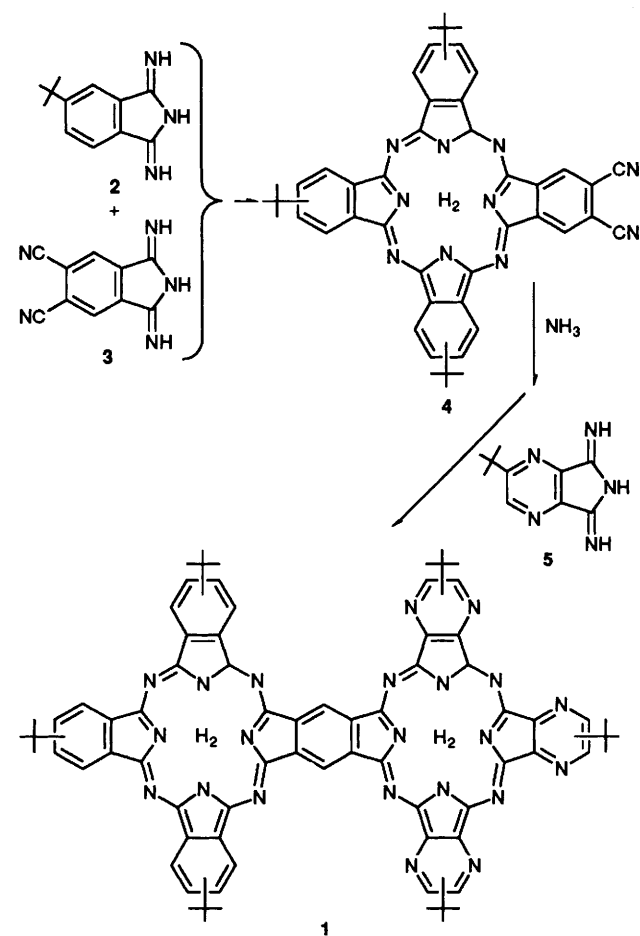
Nagao Kobayashi,* Yasuhiro Higashi and Tetsuo Osa*

Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980, Japan

A planar phthalocyanine–pyrazinoporphyrazine heterodimacrocycle and its dizinc complex have been synthesized and characterized; they are similar in several aspects to planar homodinuclear congeners but their most notable difference is a lack of fluorescence.

There has been considerable interest in the synthesis and properties of planar dinuclear porphyrins¹ and phthalocyanines² sharing a common benzene or naphthalene ring.^{2d} Although the centre–centre distance in these nucleates is *ca.* 10.7–13.0 Å (CPK molecular models), the two chromophore units interact significantly and ring- or metal-centred mixed valence species have been realized as a result.^{2a,e} Another notable point on planar dinucleation is a broadening and shift of the main absorption band to the near-IR region,^{1b,2a,e} which makes the dinucleates attractive from a practical viewpoint for photodynamic cancer therapy³ and optical disks. In this communication, we report the synthesis and some properties of the first example of a planar heterodinuclear macrocycle containing phthalocyanines or porphyrins, *i.e.* **1**, and its dizinc complex, **Zn1**, where the submacrocycles are a phthalocyanine and pyrazinoporphyrazine. As is well known, the former is an electron donor while the latter is an electron acceptor.⁴

2,2',7,7',12,12'-Tri(*tert*-butyl)benzo[*b,g,l*]-17²,17³-dicyanobenzo[*q*]-5,10,15,20-tetraazaporphine, **4**, (200 mg, 0.268 mmol), obtained from 4-*tert*-butyldiiminoisoindoline, **2**, and 4,5-dicyanodiiminoisoindoline, **3**, by mixed condensation,⁵ was treated with ammonia gas in the presence of sodium methoxide in dry dioxane–methanol (3:1 v/v, 22 ml) (Scheme 1).⁶



Scheme 1

The resultant diiminoisoindoline derivative and 2-*tert*-butyl-5,7-diimino-6*H*-pyrrolo[3,4-*b*]-pyrazine, **5**, (240 mg, 1.338 mmol) were mixed well and heated to *ca.* 230–250 °C under a nitrogen atmosphere.⁶ The crude product was imposed on a basic alumina column using methylene chloride and the blue–green fraction recovered was further purified by gel-permeation columns of Bio-beads SX2, eluting with THF. The front running dinuclear fraction was collected and recrystallized from methylene chloride–hexane to give **1** as a bluish powder (40 mg, 12%) and gave the desired parent ion peak at *m/z* = 1287 [*M* – 4H (pyrrole protons)] in the mass spectrum using FAB technique.† The dizinc derivative, **Zn1**, was obtained by refluxing **1** with excess zinc acetate in 1,2-dichloroethane–ethanol (1:1 v/v).†

Fig. 1 shows the electronic absorption and magnetic circular dichroism (MCD) spectra of **1** and **Zn1**. Both compounds show broad Soret and Q bands, with smaller absorption coefficients (ϵ) at longer wavelengths than the corresponding mononuclear control molecule, *i.e.* metal-free and zinc complexes of tetra-*tert*-butylphthalocyanine (BPC)⁷ and tetra-*tert*-butylpyrazinoporphyrazine (BPyZ).⁸ For example, the Soret and Q₀₋₀ bands of ZnBPC and ZnBPyZ lie at 349 (ϵ = 63300) and 671 nm (212500) and at 341 (57700) and 628 nm (132600), respectively, in THF. The red-shift broadening of the spectra can be explained by enlargement of the π -conjugation system plus splitting due to intramolecular exciton coupling between the two constituting sub-units in the dimers,

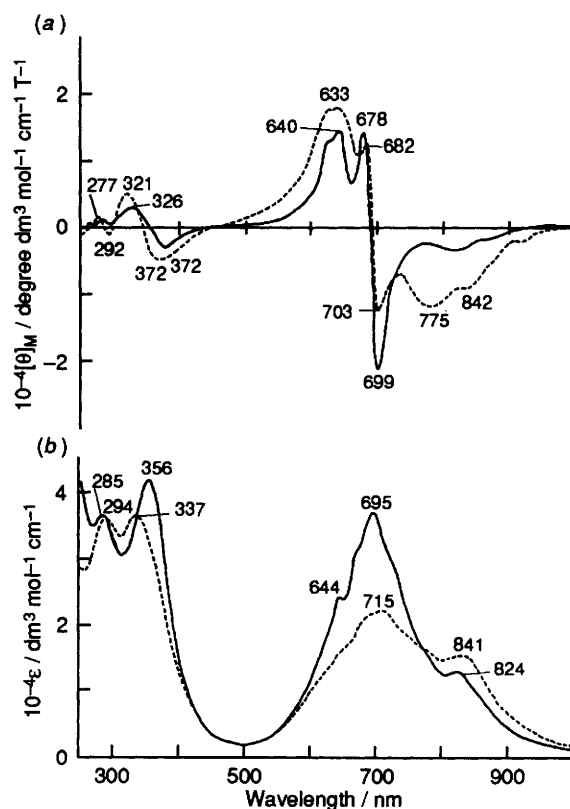


Fig. 1 (a) MCD and (b) Electronic absorption spectra of **1** (broken lines) and **Zn1** (solid lines) in THF

and/or the effect of a lowering of symmetry from the approximate D_{4h} (of BPCs and BPyZs) to the approximate D_{2h} (of **1** and **Zn1**). In addition, as in the cases of planar homodinuclear Pc^{2a} and tetrabenzoporphyrin^{1b} complexes, a weak shoulder or a peak is seen in the near-IR region. This appearance of the near-IR band is rationalized, at least theoretically,⁹ by taking a slightly bent conformation into account. The positions of the Q and near-IR bands of **Zn1** are shorter by ca. 20 nm than those of a planar homodinuclear $Pc^{2a,e}$ indicating that the effective π -conjugation system of the former is smaller than the latter. Since the Q bands of PyZs generally appear at 40–50 nm shorter wavelengths than those of Pcs¹⁰ (compare for example those above 628 and 671 nm), the value of 20 nm suggests that delocalization of the electrons is occurring to some extent over the whole molecule in **Zn1** (and **1**).

The MCD spectra can be interpreted on a similar basis. A weak broad dispersion type MCD in the main Q band region may be explained as the superimposition of two *pseudo* Faraday *A*-terms (**Zn1**) or two sets of two Faraday *B*-terms (**1**) at slightly different energies, split by exciton coupling.^{1b,2e} Their intensity is one order of magnitude smaller than that of monomeric Pcs¹¹ as a result of the cancellation of envelopes of opposite signs. A positive (negative in sign) *B*-term was observed corresponding to the weak near-IR band.

It was attempted to record fluorescence spectra by exciting in the Q band region, but no fluorescence was detected. Since the homodinuclear planar porphyrins^{1b} and Pcs^{2b} generally fluoresce with moderate intensity, this lack of fluorescence suggests very intensive intramolecular quenching due to charge-transfer from perhaps BPC to BPyZ moieties.¹²

The differential pulse voltammograms of ZnBPc, ZnBPyZ and **Zn1** were recorded in *o*-dichlorobenzene containing 0.3 mol dm⁻³ tetrabutylammonium perchlorate. The redox potentials of ZnBPy were observed at 1.03, -0.97, -1.38 and -2.14 V vs. Ag/AgCl, while those of ZnBPc were at 1.01, 0.21, -1.41 and -1.81 V, indicating that the 1st-oxidation and -reduction potentials of ZnBPyZ lie at 0.82 and 0.44 V more positive potentials than those of ZnBPc. The potential difference (ΔE) of the 1st-oxidation and -reduction in ZnBPc is 1.62 V while that in ZnBPyZ is 2.00 V. Since the corresponding value in general porphyrins is ca. 2.25 V,¹⁴ the size of the effective π -conjugation system in BPyZ is in between that of Pcs and general porphyrins. **Zn1**, on the other hand, shows couples at 1.36, 0.76, 0.50, -0.96, -1.34, -1.82 and -2.2 V. From their positions and the amount of current (smaller in positive potential region), these redox couples are not a simple superimposition of the couples of ZnBPc and ZnBPyZ; rather they might be interpreted as being caused by the interacting dipoles in different chromophore molecules. In particular, in the voltammograms of **Zn1**, there is no redox couple at 0.21 V which corresponds to the first oxidation couple of ZnBPc. Although the area of the peaks in the voltammogram is not necessarily the same, this appears to be due to the instability of the BPyZ moiety, especially since it is known that PyZ is weak against oxidation.¹³ Interestingly, the ΔE (1.78 V) between the midpotentials of the 1st- and 2nd-oxidation and 1st- and 2nd-reduction is in between ΔE of the 1st-oxidation and -reduction in ZnBPc (1.62 V) and ZnBPyZ (2.00 V). The overall shape of the voltammogram resembles that of homodinuclear planar Pc^{2e} and tetrabenzoporphyrin.^{1b}

Thus, the above data manifest that **1** and **Zn1** have several aspects similar to those of planar homodinuclear congeners, but the most pronounced difference is the lack of fluorescence. In addition, we have found several phenomena which are not seen in monomeric Pcs and homodinuclear planar molecules. For example, CoBPc, CoBPyZ and homodinuclear planar dicobalt Pc are not particularly unstable, while the pyrazinoporphyrazine moiety of **Co1** always decomposed in the course of purification after cobalt insertion reaction to **1** skeleton.

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Footnote

† Compounds **1** and **Zn1** gave satisfactory elemental analytical data. ¹H NMR δ (500 MHz; CD₂Cl₂) **1**: 6.0–9.5 (14 H, br, ar), 1.2–1.5 (54 H, m, al), -1.28 (2 H, br, pyrrole) and -3.14 (2 H, br, pyrrole). **Zn1**: 7.0–9.5 (14 H, br, ar) and 1.7–2.1 (54 H, m, al).

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