



The first phthalocyanine-based dimer formed by two pyridine-Pd-pyridine bridges

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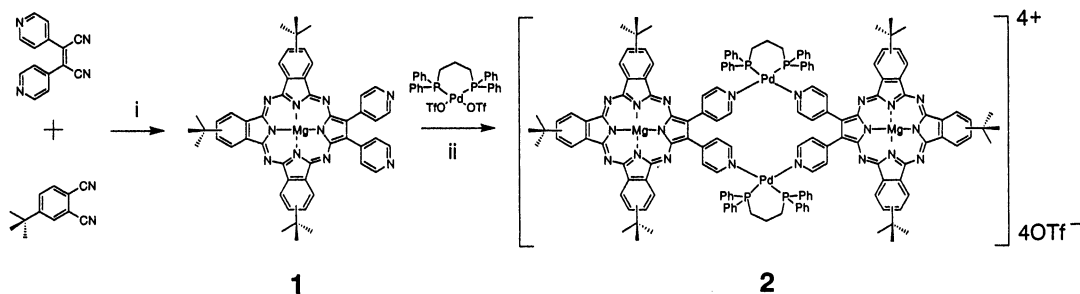
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Abstract—A phthalocyanine (Pc)-analogue containing two pyridine units is dimerized via two pyridine-Pd-pyridine bridges to form a novel type of planar or nearly planar Pc dimer. Because of the structural constraint in the constituent monomer, this dimer has a rhombic-shaped square in its center, which has not been attained previously in porphyrin-based supramolecules. © 2001 Elsevier Science Ltd. All rights reserved.

Phthalocyanine (Pc)-based planar or nearly planar dimers reported to date include those connected by a common benzene¹ or naphthalene² bridge, two butyne bridges³ or a metal.⁴ Significant intramolecular chromophore–chromophore interactions were observed in these except for the last case. We report here the first example of a fifth type of Pc-based planar dimer, which is a di-nuclear tribenzotetraazaporphyrin linked by two pyridine-Pd-pyridine bridges, **2** (Scheme 1). Several oligoporphyrins connected by coordination bonds, particularly between pyridine and palladium or platinum,^{5,6} have been reported over the past few years, but so far nobody has succeeded in synthesizing this type of Pc-based molecule. Although all oligoporphyrins reported to date make angles of either normal (90°) or linear (180°) at the bridging metal position, the angle in compound **2** appears to be between 90 and 180 degrees because of the molecular requirement of the precursor, i.e. bis-pyridine containing tribenzo[*b,g,l*]-

porphyrine **1**. Accordingly, the region surrounded by two pyridine-Pd-pyridine bridges becomes a rhombic-shaped square, which has not been attained previously in any porphyrin-based supramolecular dimers. In addition, when viewed as a special pair model in the photosynthetic reaction center, compound **2** is superior to porphyrin systems in the following two aspects. (i) The absorption spectrum is closer in shape and energy to that of chlorophylls. (ii) Pcs are more stable and robust. Furthermore, the interaction of the two chromophores in **2** would be interpreted simply, since their conjugation is prevented by the two Pd atoms.

Compound **1** could be readily prepared by a cross cyclotetramerization reaction of 4-*tert*-butyl-phthalonitrile and 2,3-bis(4-pyridyl)-2,3-dicyanomaleonitrile (obtained by the oxidative condensation of 4-pyridyl-acetonitrile⁷) in refluxing butanol/magnesium butoxide



Scheme 1. Reagents and conditions: (i) BuOH/Mg(OBu)₂, reflux, 24 h; (ii) room-temperature, 8 h.

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mixture for 1 day. After evaporation of the solvent, the residue was separated on a neutral alumina column using $\text{CHCl}_3/\text{MeOH}$ (50:1 v/v), and the second blue fraction containing the desired **1** was collected and recrystallized from $\text{CHCl}_3/\text{MeOH}$ (24%).⁸ Compound **1** was then reacted with an equal amount of bistriflate salt of 1,3-bis(diphenylphosphino)propane palladium (II) (dpppPd(II)OTf_2).⁹ (Scheme 1) Formation of the dimeric macrocycle **2** proceeded smoothly at room temperature. The blue-black microcrystalline compound **2** precipitated out of the reaction mixture upon addition of diethyl ether (74% after two precipitation). The analytical data as well as results of gel permeation chromatography (using Bio-beads SX-1 column (Bio-rad)) suggested that oligomers higher than the dimer are at a very low level if present at all in the reaction mixture, even though the anticipated angle of the macrocycle corner, formed by two pyridine moieties, is significantly wider than 90 degrees.¹⁰ In the electrospray mass (ES) spectrometry of **2**, the +1 species resulting from the loss of a proton ($m/z=3251.1$) and one triflate counterion ($m/z=3102.1$) was observed and the isotropic distribution consistent with the theoretical isotropic contributions confirmed the composition of **2**. The ^1H NMR spectra of **1** and **2** could not be compared in the same solvent, although it is desirable to use the same solvent. Compound **1** gave the clearest spectrum in d_6 -DMSO among common solvents, while in CD_2Cl_2 or CDCl_3 the spectrum became more complex by broadening, plausibly because of the higher tendency of Pc analogues to aggregate¹¹ and the presence of polar pyridyl groups. The dimer **2**, on the other hand, showed relatively good signals in CD_2Cl_2 , plausibly because the polar pyridyl groups in **1** were blocked by Pd atoms carrying large hydrophobic ligands, and analysis of the integrated intensities supported the dimer structure. However, clear signals were not obtained in DMSO, DMF and acetone, although in some cases of porphyrin-based supramolecules^{5a} it is known that polar solvents give better resolved signals. Since the differences of **1** and **2** should appear in the vicinity of the pyridine-Pd-pyridine bridge, we directed our attention to the phosphorus atoms next to Pd. Fortunately, the pronounced shift in the ^{31}P NMR of **2**

($\delta=8.3$ in CD_2Cl_2) compared to dpppPd(OTf)_2 ($\delta=20.0$)⁹ clearly suggested that Pd-containing fragments are coordinated to the tribenzo[*b,g,l*]porphyrazine core via pyridyl nitrogen atoms.¹⁰

As in many other porphyrin-based supramolecules containing bridges constituting pyridine and Pd or Pt atoms,⁵ **2** is more soluble than the precursor **1**, which has a low solubility in common solvents, and this fact may be explained by prevention of intermolecular stacking due to the positive charge and bulky eight phenyl groups as the phosphine ligands in **2**.

Fig. 1 shows the electronic absorption and magnetic circular dichroism (MCD) spectra of **1** and **2**. The well-split two-peak Q bands in the absorption spectra of **1** and **2** are characteristic of the tribenzo[*b,g,l*]porphyrazine chromophore,¹² and therefore suggest that π conjugation through the linking pyridine-Pd-pyridine bridge is small. The MCD spectra of **1** and **2** are characteristic of unsymmetrical (with C_{2v} effective symmetry of chromophores) phthalocyanines and their analogues, producing Faraday *B*-terms corresponding approximately to the absorption maxima or shoulders.¹³ From the inversion of the sign of the *B*-terms,^{13,14} two strong Q band peaks in **1** and **2** obviously belong to the Q_x and Q_y transitions. The maxima of the Soret and Q_x bands are red-shifted by 2 and 25 nm, respectively, in **2** compared to those of the starting complex **1**. This shift of the absorption peaks to longer wavelength on dimer formation is similar to the trend seen in porphyrin systems with pyridine-Pt or -Pd bridges.⁵ On the other hand, the maximum of the Q_y band is blue-shifted by 12 nm and the splitting of the Q_x - Q_y bands in **2** is larger by 37 nm than in **1**. As in the case of porphyrin-based supramolecular dimers and oligomers,^{5,6} the Soret, Q_x , and Q_y bands of **2** are broader compared to those of the precursor **1**, probably because of intramolecular exciton coupling between the tribenzo[*b,g,l*]porphyrazine chromophores. The extinction coefficient per tribenzo[*b,g,l*]porphyrazine unit decreases by approximately 20% upon formation of **2**, again in close similarity with the porphyrin systems.^{5,6}

In conclusion, we have reported the first nearly planar dimer of a Pc-analog linked by two pyridine-Pd-pyridine bridges. The region surrounded by two Pc analogues is rhombic, which has not been realized previously in any porphyrin-based molecules. Synthesis of other metal-induced self-assembled supramolecules based on a tribenzo[*b,g,l*]porphyrazine core is in progress.

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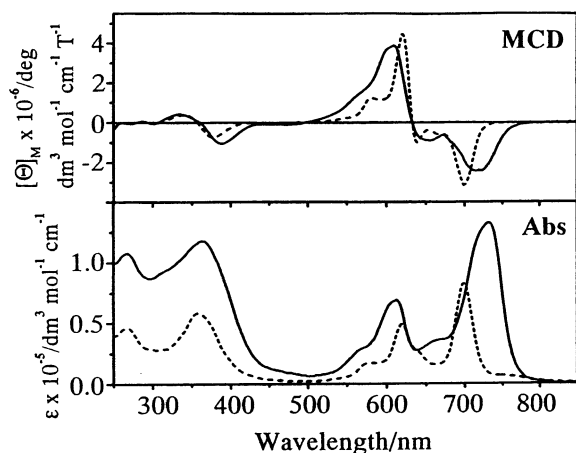


Fig. 1. Absorption and MCD spectra of **1** (broken lines) and **2** (solid lines) in chloroform.

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8. Anal. Calcd for $C_{50}H_{44}N_{10}Mg \cdot 2H_2O$: C, 71.09; H, 5.69; N, 16.59%. Found: C, 70.54; H, 5.71; N, 16.03%. MS (ES) m/z 809.3 (M+H)⁺ calcd 809.4. ¹H NMR (dms-*d*₆, 400 MHz): δ 9.38–9.21, 9.05–8.97 (6H, Pc), 8.92 (4H, Py), 8.37–8.28 (3H, Pc), 8.22 (4H, Py), 1.74–1.67 (27H, *t*-Bu). UV–Vis [λ , nm (lg ϵ)] in CHCl₃: 702 (4.92), 642sh, 622 (4.69), 575sh, 376sh, 359 (4.76).
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