A Novel Naphthalocyanine Isomer: A Dinaphthophthalocyanine with C_{2v} Symmetry

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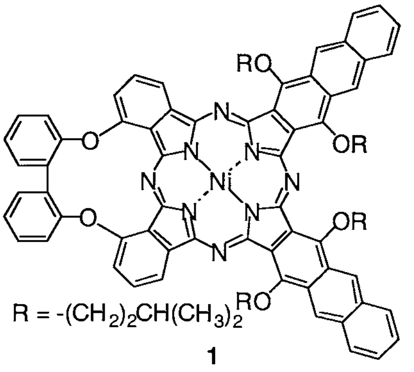
An adjacently dinaphtho-substituted phthalocyanine with C_{2v} symmetry, which is a structural isomer of naphthalocyanines in the sense that eight benzene units are fused to the tetraazaporphyrin skeleton, has been synthesized and characterized by electronic absorption and magnetic circular dichroism spectroscopy, and molecular orbital calculations within the framework of the ZINDO approximation.

Naphthalocyanines (Ncs) are compounds in which a benzene ring is fused to each of the four benzene rings of phthalocyanines (Pcs), and two structural isomers, i.e. linearly benzoannulated 2,3-Nc and angularly benzoannulated 1,2-Nc are generally known. In particular, the former shows strong electronic absorption bands in the near-IR region, so that much attention has been focused on using the Nc derivatives as photosensitizers in conjunction with lasers in areas such as the photodynamic therapy of cancers.[1] However, no other Ncs or Nc isomers have been reported to date. The appearance of new Ncs will not only be beneficial in applied fields, but also attractive from the viewpoint of comparison with hitherto known Ncs. From this respect, we decided to synthesize a new type of Nc isomer, utilizing knowledge accummulated in Pc chemistry. Although normal metalloPcs have π-systems with D_{4h} symmetry and show a single intense Q band, adjacently di-substituted Pc derivatives (adj-Pcs) with C_{2v} symmetry are also predicted to have a single intense maximum in the Q band region by the symmetry-adapted perturbation (SAP) method,[2,3] and indeed these kinds of adj-Pcs have been reported.[4-9] Recently, we have reported the selective synthesis of adj-Pcs.[10] Accordingly, by combining the above C_{2v} symmetry concept and the selective synthetic method, we now report the synthesis and spectroscopic properties of a novel low-symmetrical Pc with two fused naphthalene units at the adjacent benzene rings (compound **1**). This is considered to be a structural isomer of Nc in the sense that eight benzene units are fused to the tetraazaporphyrin skeleton. The detailed method of the synthesis of compound **1** is described in the Footnotes.[11]



R = $-(CH_2)_2CH(CH_3)_2$

1

Figure 1 shows the electronic absorption and magnetic circular dichroism (MCD) spectra of **1** in toluene, together with those of Nickel(II) 5,9,14,18,23,27,32,36-octabutoxy-2,3-naphthalocyanine (**2**, purchased from Aldrich Chemical Co. and purified.), which is suitable for comparison with **1** because of the substitution of similar positions by alkoxy groups. Clearly, we can see that both spectra are very similar in shape, although there are some shifts in the wavelengths. Compound **1** as well as **2** has a single Q_{0-0} absorption band and a corresponding distinctive Faraday *A* term in the MCD spectrum. The bandwidths at half height of the Q_{0-0} band are 505 cm^{-1} for **1** and 590 cm^{-1} for **2**. The Q band of **2** is, of course, theoretically doubly degenerate,[12] but the Q bandwidth of **1** is even smaller, suggesting that its Q band is also accidentally degenerate, although, strictly speaking, any excited states cannot be degenerate in C_{2v} systems. The Q band peak of **1** appears at shorter wavelength (799 nm) than that of **2** (846 nm). Most of this difference (47 nm) can be reasonably explained as a substituent effect of the alkoxy groups. Substituent effects depend on the type and number of substituent groups, and an approximate additivity exists when the same substituent is introduced at the same position of fused aromatics.[13,14] Calculating from the substituent effect of alkoxy groups,[14] the Q_{0-0} band peaks of **1** and **2** without substituents may appear at ca. 735 ± 8 and 745 ± 10 nm, respectively.

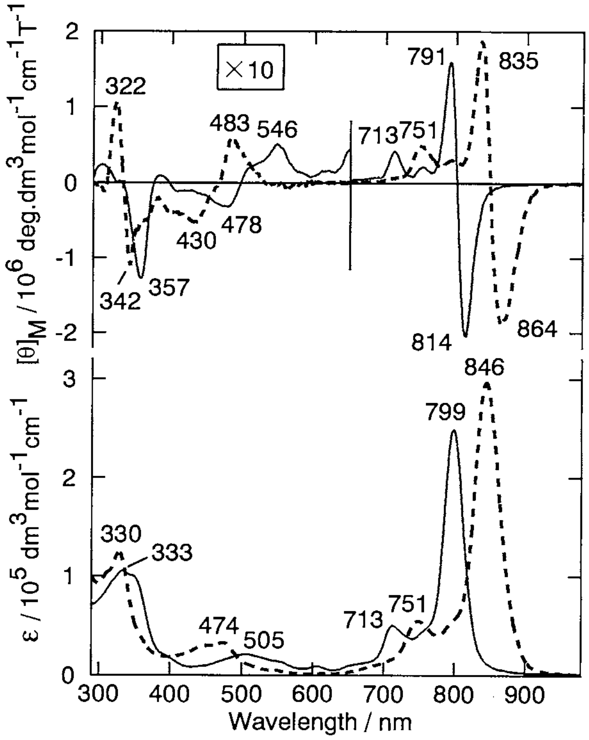


Figure 1. MCD (top) and electronic absorption (bottom) spectra of **1** (Solid line) and **2** (dotted line) in toluene.

Some broad bands are observed in the region between the Q and Soret bands, at around 450-600 nm for **1** and 400-500 nm for **2**. In Ncs, similar bands are generally seen, and are assigned as local excitations on naphthalene rings.[4] Therefore, in the case of **1**, the band in the 450-600 nm range may be similarly assigned as local excitations on anthracene rings.

In order to deepen our interpretation of the spectra of **1** and **2**, their molecular orbital calculations were carried out using the ZINDO/S program[15-17] (peripheral substituents were, however, removed). For **1**, the two split Q bands were estimated to lie at 756 nm (13230 $\mathrm{cm^{-1}}$, f = 1.118) and 747 nm (13383 $\mathrm{cm^{-1}}$, f = 1.247), whereas the doubly degenerate Q band of **2** was calculated to lie at 763 nm (13100 $\mathrm{cm^{-1}}$, $f = 1.263 \times 2$). In the case of **1**, the energy difference between the two split Q bands is 153 $\mathrm{cm^{-1}}$, which is about one-third of the bandwidth at half height of the observed Q band of **1**, so that the Q band of **1** is almost doubly degenerate. This seems to be the reason that we observed a single Q band experimentally (Figure 1). In addition, the above results reproduce accurately the relative Q band intensity and position between **1** and **2**. That is, the Q band (*ca.* 630-980 nm) intensity ratio of **1** to **2** is experimentally 0.80 (f = 1.00 for **1** and 1.24 for **2**) for the thoretical *ca.* 0.94 $\{= (1.118 + 1.247)/1.263 \times 2\}$, and the estimated (by removing substituent effect) Q band position of the π structure of **1** (735 nm), which is shorter than that of **2** (745 nm) by 10 nm, was reproduced as *ca.* 13 nm.

Moreover, the calculations predict doubly degenerate HOMO→LUMO+3 (naphthalene-centered orbital) transitions at 455 nm (21983 $\mathrm{cm^{-1}}$, $f = 0.072 \times 2$) for the π structure of **2**, and HOMO→LUMO+2 and LUMO+3 (anthracene-centered orbitals) transitions at 549 nm (18207 $\mathrm{cm^{-1}}$, f = 0.147) and 504 nm (19831 $\mathrm{cm^{-1}}$, f = 0.039), respectively, for the π structure of **1**. These are also in agreement with the observed trends with respect to both intensity and positions of the bands.

In summary, we have synthesized and identified a novel naphthalocyanine isomer, dinaphthophthalocyanine with C_{2v} symmetry, that has an intense Q band in the near-IR region for the first time. The spectroscopic properties were well-reproduced and explained by MO calculations using the ZINDO/S program. All data indicate that an adjacently dinaphtho-substituted Pc can be indeed regarded as a new Nc isomer.

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11 2,3-Dicyano-1,4-diisopentoxyanthracene. To a mixture of 2,3-dicyano-1,4-dihydroxyanthracene[18] (9 g, 34 mmol) and K_2CO_3 (19 g, 137 mmol) in N,N-dimethylacetamide (70 ml) was added isoamyl iodide (13.5 ml, 103 mmol). The mixture was heated to reflux for 4d, the solvent was removed *in vacuo*, and the residue was chromatographed on a silica gel column with toluene. The bright yellow product was collected, then recrystallized from MeOH, to give 3 g (22% yield) of the title compound. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm 8.79 (S, 2H), 8.11 (m, 2H), 7.68 (m, 2H), 4.61 (t, 4H), 1.98 (m, 6H), 1.06 (d, 12H). IR $\nu_{max}/\mathrm{cm^{-1}}$(KBr): 2217 (CN). m.p. 143-145 °C. Anal. Calcd for $C_{26}H_{28}N_2O_2$: C, 77.97; H, 7.05; N, 6.99%. Found: C, 77.79; H, 6.97; N, 6.82%.
Compound **1**. Under N_2, a mixture of 2.3-dicyano-1,4-diisopentoxyanthracene (160 mg, 0.4 mmol), 2,2'-bis(2,3-dicyanophenoxy)biphenyl[9] (85 mg, 0.2 mmol), and isopentyl alcohol (4 ml) treated with Li (6 mg) was heated to reflux for 1h. $NiCl_2$ was added to the mixture, which was stirred for a further 1h. The solvent was removed *in vacuo* and the residue was chromatographed on a silica gel column with toluene-hexane (1:1 v/v). Further purification was performed by GPC on Bio-beads gel (S-X1). The dark purple product was collected, then recrystallized from CH_2Cl_2-petroleum ether, to give 7 mg (2.7% yield) of the title compound. ^{1}H NMR (400 MHz, CD_2Cl_2): δ/ppm 7.1-8.4 (m, 26H, arom), 4.9-5.2 (m, 8H, $-OCH_2-$), 1.9-2.5 (m, 12H, $-CH_2CH-$), 0.9-1.2 (m, 24H, CH_3); FAB-MS m/z (relative intensity) 1297 (M^+, 68), 1227 ($[M-1R]^+$, 10), 1014 ($[M-4R]^+$, 100); Anal. Calcd for $C_{80}H_{70}N_8O_6Ni$: C, 74.02; H, 5.44; N, 8.63%. Found: C, 73.81; H, 5.56; N, 8.59%.
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