

Efficient Synthesis of a Donor-Acceptor Phthalocyanine Having Adjacent-Fused Pyrazine Rings

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Condensation reaction of 3,6-diphenylphthalonitrile and 2,3-dicyano-5,6-diethyl-1,4-pyrazine employing the modified lithium method has efficiently produced the novel donor-acceptor phthalocyanine derivatives having adjacently-fused pyrazine rings.

Phthalocyanines (Pcs) and their related macrocyclic π -delocalized molecules such as subphthalocyanines continue to attract considerable attention because of their potential usefulness for molecular devices, electrical conductors, nonlinear optical (NLO) materials, and so forth.¹ In particular, Pcs exhibiting large second-order nonlinearities have been pursued in recent years from both the synthetic and photophysical viewpoints, due to their applicability in frequency doubling, parametric oscillation, and high-speed light modulation.² One theoretically predicted structural candidate for second-order NLO materials is a Pc possessing, adjacently, two donor (D) and two acceptor (A) groups, in order to induce a large intramolecular polarizability.³ On the basis of these theoretical results, many attempts at synthesizing adjacently di-substituted donor-acceptor Pc system (AADD)⁴ have been made, but no-one has ever succeeded in obtaining the desired products. Therefore, the elucidation of the second-order NLO properties has been limited to mono-acceptor-substituted Pcs (ADDD).⁵ The difficulty in synthesizing the AADD type Pcs is probably due to the very different reactivities of the two types of starting material, i.e. *o*-dinitrile derivatives. It is empirically known that *o*-dinitriles containing strong electron-withdrawing groups such as sulfone or nitro groups are too reactive to co-macrocyclize with other *o*-dinitriles having electron-releasing groups. As a result, even if the two types of *o*-dinitrile, i.e. donor and acceptor units, are mixed well and reacted for a time, the acceptor units react predominantly by themselves, to form AAAA or AAAD derivatives and, therefore, an AADD type is not obtained. In the present study, we have achieved highly efficient synthesis of the AADD type Pc derivative using 3,6-diphenylphthalonitrile **1** as donor and 2,3-dicyano-5,6-diethyl-1,4-pyrazine **3** as acceptor molecules.^{6,7}

The main feature of the synthesis was the employment of the so-called lithium method and nitrile **1** containing two protruding phenyl groups.⁸⁻¹⁰ At first, **1** only was reacted with lithium hexyl oxide at 170 °C for a while, to form the speculated intermediate **2**. Since the phenyl groups of phthalonitrile are significantly crowded for the Pc synthesis, the formation of the DDDD derivative did not proceed effectively during the first stage of the reaction.¹¹ Subsequently, stepwise addition of **3** led to a rapid reaction between **2** and **3** (Scheme 1). Figure 1 shows the relative yields of the resultant five compounds and the AAAA. Each compound was characterized by ESI-TOF mass, NMR, and elemental analysis.¹² From this figure, it is clear that the yield of the AADD is far above that of the other five derivatives. As noted above, since the phenyl groups surpass the formation of DDDD and ADDD, the yields of DDDD and ADDD are only 2 and 21%, respectively, relative to that of the AADD derivative. Moreover, since pyrazinoporphyrinazines cannot be synthesized from 2,3-dicyano-1,4-pyrazine by the lithium method,¹³ the yield of the AAAA derivative was nil or negligible. Thus, our proper selection of donor **1**, acceptor **3**, and the macrocyclization method functioned effectively in inhibiting the formation of the DDDD, ADDD, and AAAA type derivatives. Interestingly, the relative yield of ADAD is only 9% of AADD, although these are structural isomers to each other. This strongly suggests that our speculated intermediate **2** was indeed formed in the course of the synthetic process and predominantly reacted with **3**, although this kind of

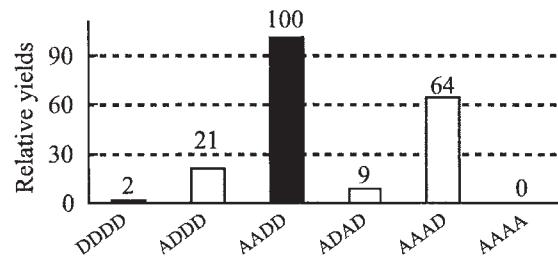
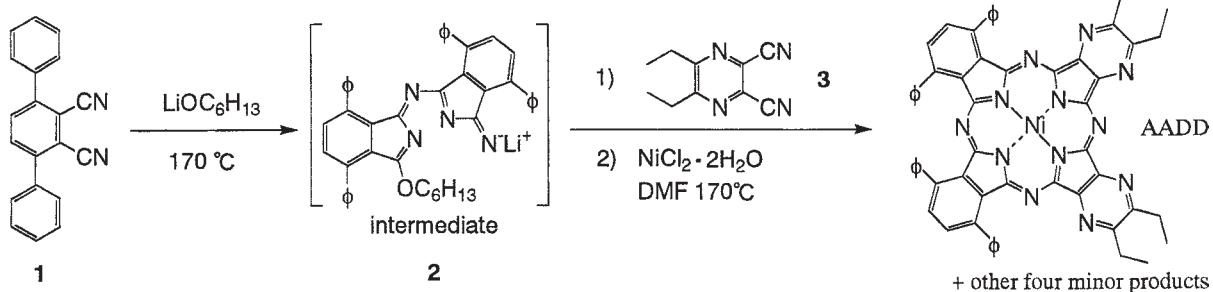


Figure 1. Relative yields based on molar ratios of the products.



Scheme 1. Proposed mechanism for the predominant formation of AADD.

“half Pc” intermediate is isolable only in the limited cases.¹⁴

Figure 2 shows the ¹H NMR spectra for the aliphatic proton regions of AADD in CDCl₃. In fact, mass spectra and elemental analysis were insufficient for the structural determination of the AADD type because ADAD is an isomer of this. In Figure 2, however, slightly shifted and overlapping quartet and triplet signals are seen at ca. 3.40 and 3.35, and at 1.71 and 1.68 ppm, respectively. The superimposed triplets were further analyzed utilizing a curve fitting technique, as shown in the figure. A complex spectral envelope from the ca. 1.73 to 1.66 ppm region is composed of two overlapping triplet signals at 1.71 and 1.68 ppm. Therefore, it is clear that the AADD derivative has two types of ethyl group, which are surrounded by different chemical environments. Conversely, if our assignments were not correct and the AADD derivative was actually an opposite isomer, that is ADAD, its four ethyl groups would be in exactly the same chemical environment because of its D_{2h} molecular symmetry, and would therefore appear as single quartet and triplet signals. As illustrated in the inset of Figure 2, the ¹H NMR spectra of ADAD are comprised of single quartet and triplet signals at 3.32 and 1.67 ppm, respectively. As a result, the AADD structure of the compound in this study can be confirmed. The ¹³C NMR spectrum also supports the above conclusion; each signal originating from both the methyl (12.92 and 12.79 ppm) and methylene (29.04 and 28.82 ppm)¹⁵ carbons splits into two components, indicating the presence of C_{2v}, not D_{2h}, symmetry of the AADD.

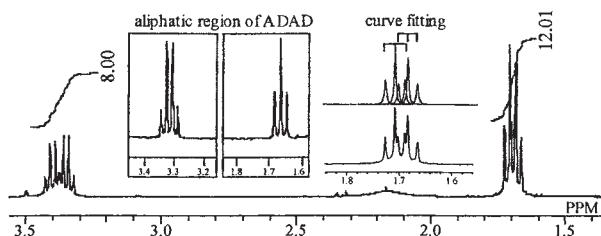


Figure 2. ¹H NMR of AADD and its curve fitting result. Only aliphatic region is shown. The inset shows the corresponding region of the AADD isomer.

AADD showed an unsplit Q-band at 680 nm in chloroform, which is energetically approximately midway between AAAA (626 nm) and DDDD (752 nm). The shape of the Q-band was typical for adjacently di-substituted Pc derivatives¹⁶ and the corresponding magnetic circular dichroism signal was a dispersion type quasi Faraday A term. The first oxidation and reduction potentials of AADD were +0.45 and -1.33 V (vs Fc/Fc⁺), respectively, in *o*-dichlorobenzene, which also showed an intermediate character between AAAA and DDDD. These observations indicate substituted donors and acceptors worked additively.

In summary, we have described the synthesis of a novel, and previously unobtainable, Pc-based donor-acceptor system realized from **1** and **3**, by employing an improved lithium method. We anticipate that phthalonitriles having bulky substituents at the 3 and 6 positions are useful for controlling the geometrical structures (two dimensional electronic structures) of Pc derivatives.

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References and Notes

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- AADD: Lithium (10 mg, 1.4 mmol) was heated at 100 °C in 1-hexanol (3 mL) until all of the metal was dissolved. After cooling to room temperature, **1**⁹ (1 g, 3.57 mmol) was added and reacted for ca. 3 min at 170 °C, to give a yellowish green solution. Keeping the reactor at 170 °C, nitrile **3**¹⁰ (1 g, 5.37 mmol) dissolved in hot 1-hexanol (ca. 3 mL) was added dropwise via a syringe. The solution immediately turned to dark blue, and the reaction was continued for a further 1 h. After boiling off most of the solvent, DMF (20 mL) and NiCl₂·2H₂O (3.7 g, 22 mmol, 10 equiv) were added, and kept at 170 °C for 30 min. The mixture was then poured into water, and the resultant solid filtered off, washed with water and methanol, and dried under vacuum. The residue was briefly passed through a short column (silica, CHCl₃-methanol (20 : 1 v/v)) and the obtained blue mixture further purified by column chromatography (silica, toluene-methanol (1 : 0 – 30 : 1 v/v)), to give 3.5, 35, 151, 14, and 87 mg of the DDDD, AADD, AADD, ADAD, and AAAD, respectively. Spectral data for AADD: Mass(ESI-TOF): *m/z* 990 (M⁺); elemental Anal. calcd for C₆₀H₄₄N₁₂·H₂O: C, 71.37; H, 4.59, N, 16.65%. Found: C, 71.46; H, 4.78; N, 16.35%. δ _H (400 MHz, CDCl₃): 1.68 (t, *J* 8 Hz, 6H), 1.71 (t, *J* 8 Hz, 6H), 3.35 (q, *J* 8 Hz, 4H), 3.40 (q, *J* 8 Hz, 4H), 7.27 (dd, 4H), 7.34 (dd, 2H), 7.42 (d, 4H), 7.74 (dd, 2H), 7.80 (d, *J* 8 Hz, 2H), 7.81 (dd, 4H), 7.95 (d, *J* 8 Hz, 2H), 8.21 (d, 4H). UV-vis (CHCl₃): λ_{max} = 680 nm (ϵ = 110000 M⁻¹cm⁻¹), 610 (25000), 353 (sh), 312 (67000).
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