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The first synthesis of a gable bis-phthalocyanine

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Abstract—A gable type bis-phthalocyanine (Pc) has been synthesized for the first time using a bis-phthalonitrile unit synthesized in three steps. This Pc dimer has a fluorescene quantum yield that is not significantly reduced relative to that of the control Pc monomer.

Various types of phthalocyanine (Pc) dimers have been reported to date,[1] including cofacial sandwich type lanthanide complexes,[2] μ-oxo dimers,[3] and coplanar homo-[4] and heterodimers.[5] However, no report has appeared previously on angular Pc dimers, such as the gable bis-Pc reported in this communication. The key intermediate unit during the synthesis is a gable type of bis-phthalonitrile, which provides the bridging unit for connecting the two Pc rings. Florey and Vogel[6] reported the synthesis of compound **1**, which can be transformed to bis-phthalonitrile derivative **2** by reaction with dicyanoacetylene. Compound **1** can be synthesized from commercially available cyclopentadiene and maleic anhydride by a nine-step reaction in about 0.15% yield.[6,7] A similar connecting unit, compound **8**, may be prepared by the route shown in Chart 1. However the starting material, bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride **3** is prohibitively expensive, and dicyanoacetylene is highly toxic and cannot easily be obtained in large scale quantities.[8] Judging from the typical reaction yield in each step, the final linking unit, compound **8**, would be obtained in only ca. 5–8% yield from starting compound **3**. Our aim therefore has been to prepare the connecting unit using a shorter, more generally applicable synthetic method. In this communication, we report the efficient synthesis of a type of gable bis-phthalonitrile, compound **11**, and the gable Pc **12** that can be derived from it.

In order to obtain a gable type bis-phthalonitrile by the shortest route (three steps, Chart 1 bottom), anthracene and *cis*-2-butene-1,4-diol were reacted to form *d*,*l*-2,3(9,10-anthrylene)-1,4-butandiol, **9**.[9] In order to introduce four bromine atoms, **9** was added to an ice-cooled mixture of bromine and iodine (ca. 1000:1 molar ratio) over the period of 1 h.[10] The reaction was then continued in the dark for 6 h at 0 °C and then for 18 h at room temperature. After workup with $Na_2S_2O_3$ aqueous solution, and column chromatography using basic alumina and $CHCl_3$, tetra-brominated **10** was obtained in ca. 70% yield.[11]

Cyanation of polybrominated (and polyiodinated) aromatic compounds is challenging. Several different methods have been proposed. The most well known is the Rosenmund–von Braun reaction of aromatic poly-brominated or -iodinated compounds.[12] However, there are no reports of successful substitution of complexes with more than three bromine or iodine atoms using this method. Application to compound **9** produced a mixture of mono-, di-, and tri-cyanated derivatives, with the desired tetra-substituted compound only present in less than 0.1% yield. Recently, two new methods have been reported for the cyanation of aromatic bromine atoms. In one report, substitution was carried out with reactive aryl iodide generated in situ,[13] but this method was not applied to polybrominated aromatic compounds. When we applied this method using the method described to our system, **11** was not obtained. Attempts to modify the conditions by using different solvents, and different reaction times and temperatures proved unsuccessful. In another report,[14] substitution of six bromine atoms of 2,3,6,7,10,11-hexabromotriphenylene was achieved by reacting with potassium cyanide in 2-chloronaphthalene in the presence of dibenzo-18-crown-6 and a huge excess of tetrakis(triphenylphosphine)palladium(0) catalyst at 140 °C. We studied

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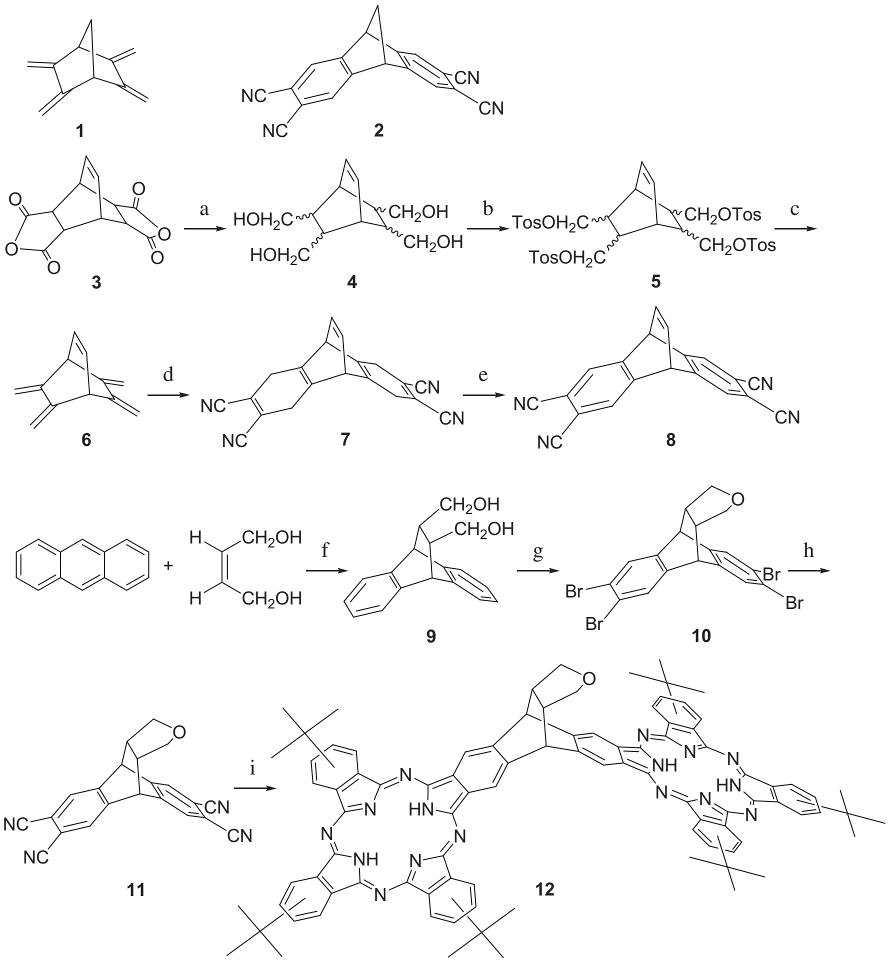

Chart 1. Structures of compounds **1** and **2**, and synthetic routes to compounds **8** (middle) and **11** and gable Pc **12** (bottom). Reagents and conditions: (a) lithium aluminum hydride, tetrahydrofuran; (b) *p*-toluenesulfonyl chloride, pyridine; (c) potassium *tert*-butoxide, dimethylsulfoxide; (d) dicyanoacetylene; (e) 2,3-dichloro-5,6-dicyano-1,4-benzoquinone; (f) 180–185 °C; (g) bromine, iodine; (h) KCN, [Pd(PPh_3)$_4$], *N*,*N*-dimethylformamide; (i) 4-*tert*-butylphthalonitrile, lithium, 1-pentanol.

the latter method in detail and systematically modified the amount of catalyst, the solvent, and the reaction time and temperature to maximize the yield. We were eventually able to obtain compound **11** in ca. 50–55% yield using this method.[15] The presence of dibenzo-18-crown-6 does not affect the reaction yield, but increases the complexity of the purification step of the resulting compound. The tetrakis(triphenylphosphine)palladium(0) catalyst starts to decompose at temperatures as low as 110–120 °C, so a very large excess has to be present within the system. In addition to the high total yield (>20%), there are several advantages to this approach. No mono- and di-cyanated compounds were obtained, and a slight trace of tri-cyanated compounds that was formed could be easily removed with a recrystallization step. The synthetic route is short and involves no highly toxic reagents such as dicyanoacetylene.[8] The reagents are all relatively inexpensive.

Gable phthalocyanine complex, **12**, was obtained by reacting bis-phthalonitrile **11** with excess 4-*tert*-butylphthalonitrile in 1-pentanol under reflux in the presence of lithium.[16] A size-exclusion column (Bio-beads SX-1, Bio-rad) was used for product purification.[17] The absorption, magnetic circular dichroism (MCD), fluorescence emission, and excitation spectra (Fig. 1) were similar to those of monomeric Pcs, indicating that the level of interaction between the two Pc units is limited. The most notable point is that the quantum yield (Φ_F) of fluorescence emission (=0.55) is not reduced significantly relative to that of the monomer (=0.76). This is a unique property that has not previously been observed in any dimeric Pc system and provides strong evidence that the two Pc units in the dimer are not conjugated and that cofacial aggregation of Pc units may be suppressed by the gable type conformation.[18] The dihedral angle of the two Pc rings was predicted to be ca. 105° for the zinc derivative on the basis of a geometry optimization using the PM3 Hamiltonian. It should be noted that the Stokes shift is small, suggesting that the structure is conformationally rigid.

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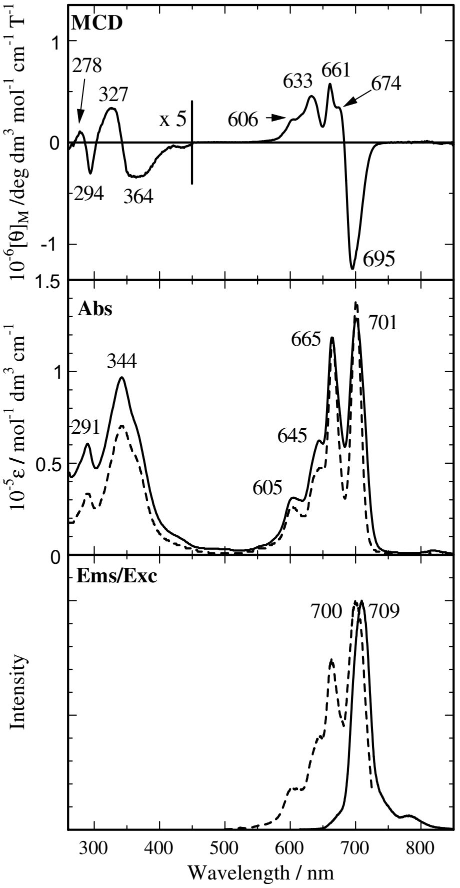

Figure 1. MCD (top), electronic absorption (middle) spectra of tetra-*tert*-butylated H_2Pc monomer (broken line) and gable Pc **12** (solid line), and fluorescence emission (solid line) and excitation (broken line) spectra of **12** (bottom) in $CHCl_3$.

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11. The following represents a typical procedure for the bromination of **10**: to an ice-cooled mixture of bromine (8 mL, 156 mmol) and iodine (41 mg, 0.16 mmol) was added *d,l*-2,3(9,10-anthrylene)-1,4-butandiol, **9** (3.70 g, 13.9 mmol) in small portions over the period of an hour. The reaction vessel was shielded from light and the reaction continued for 6 h in an ice-cooled bath and then for 18 h at room temperature. The reaction mixture was dissolved in CH_2Cl_2 (500 mL) and washed with water (150 mL × 2), 1 M $NaHCO_3$ (150 × 2), 10% $Na_2S_2O_3$ (150 mL × 2), and water (150 mL × 2). The organic layer was dried with $MgSO_4$ and the solvent was removed under reduced pressure to leave an orange oily liquid. Chromatography of the oily portion was carried out using basic alumina with $CHCl_3$ as the eluent resulting in three spots ($R_f = 0.860$ (yellow), 0.279 (yellow), 0.00 (red)). The portion of $R_f = 0.860$ was collected and the $CHCl_3$ was removed. Boiling hexane was added to the residual yellow oil and the mixture triturated with a glass bar to produce 5.30 g (68%) of tan yellow white crystals. For analytical purpose, this crystal was further purified using silica-gel chromatography ($CHCl_3$) to give white crystals of the desired compound. ^1H NMR (400 MHz, $CDCl_3$): δ 2.75 (m, 2H, CH), 3.36 (m, 2H, $-CH_2-O-$), 3.68 (m, 2H, $-CH_2-O-$), 4.11 (m, 2H, bridgehead), 7.51 (m, 4H, aromatic). MS (ESI-TOF): *m/z* calcd for $C_{18}H_{13}OBr_4Na^+$: 588.6 $[M-e+H+Na]^+$, found: 588.8. Calcd for $C_{18}H_{12}OBr_4$: C, 38.3; H, 2.14; N, 0.00; Found: C, 38.2; H, 2.15; N, 0.00.
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15. The following represents a typical procedure for the synthesis of **11**: to DMF (40 mL), finely ground **10** (3.01 g, 5.34 mmol), finely ground KCN (1.61 g, 24.7 mmol), tetrakis(triphenylphosphine) palladium(0) (3.70 g, 3.20 mmol) are added in this order, and nitrogen gas was bubbled for 65 min at room temperature, followed by refluxing of 75 min. The resultant black precipitate was filtered off, and the filtrate was added to an excess of MeOH to give a brown precipitate. The precipitate was washed with chloroform to give a gray precipitate of **11** (0.976 g,

52%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.78 (br, 2H, CH), 3.41 (br, 4H, –CH$_2$–O–), 4.81 (br, 2H, bridgehead), 8.147 (s, 2H, aromatic), 8.152 (s, 2H, aromatic). ^{13}C NMR (100 MHz, DMSO-d_6): δ 44.6, 46.4, 69.9, 112.6, 112.8, 116.0, 116.1, 130.0, 130.2, 146.0, 147.1. IR (KBr): 2233.8 cm^{-1} (CN). MS (ESI-TOF): *m/z* calcd for $C_{22}H_{13}N_4ONa^+$: 372.1 $[M-e+H+Na]^+$, found: 372.3. Calcd for $C_{22}H_{12}N_4O(H_2O)_{0.5}$: C, 73.9; H, 3.67; N, 15.7; Found: C, 73.6; H, 3.68; N, 15.5.

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17. The following represents a typical procedure for the synthesis of gable Pc **12**: under nitrogen, a small portion of lithium was dissolved in 1-pentanol, which had been dehydrated by Na (1 mL) at 100 °C. After cooling to room temperature, **11** (25 mg, 0.072 mmol) and 4-*tert*-butylphthalonitrile (159 mg, 0.86 mmol) were added and the whole mixture was then reacted at 150 °C (bath temperature) for 2 h with a cooler and then without the cooler at the same temperature and time to remove the solvent under nitrogen. After cooling, MeOH containing aliquots of concentrated HCl was added, resulting in a blue precipitate, which was collected by filtration with a membrane filter, and then washed with MeOH. The products contained within the precipitate were separated by size-exclusion chromatography (Bio-beads SX-1, Bio-rad) using CHCl$_3$–MeOH (10:1 v/v). Of the six bands observed on the column, the second and third bands were collected and crystallized from CHCl$_3$–MeOH to give a blue powder of the desired gable Pc **12** (2 mg, 1.9%). ^{1}H NMR (400 MHz, CDCl$_3$): δ −2.5 to −0.9 (br, 2H, pyrrole N), 1.8–2.0 (br, 54H, *tert*-butyl), 3.23 (m, 2H, CH), 3.6–4.0 (d, 4H, –CH$_2$–O–), 5.08 (br, 2H, bridgehead), 8.0–8.5 (br, 16H, aromatic). MS (MALDI-TOF): *m/z* calcd for $C_{94}H_{88}N_{16}O+$: 1457.8 $[M]^+$, found: 1458.2, *m/z* calcd for $C_{90}H_{82}N_{16}^{+}$: 1387.7 $[M-C_4H_6O]^+$, found: 1387.9.
18. Beer's law experiments were carried out for tetra-*tert*-butylated H$_2$Pc and **12** in CHCl$_3$ and CHCl$_3$–MeOH solvent mixtures. In CHCl$_3$, the results for the monomer and **12** remained linear up to 10^{-4} mol/L. In CHCl$_3$–MeOH (1:1, 1:2, and 1:3 v/v), the Q band of both systems broadened slightly to a seemingly similar extent relative to the CHCl$_3$ solutions. Under these conditions, no difference could be detected between the control monomer system and **12** between 0 and 10^{-4} mol/L.