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Synthesis and Crystal Structure of a Calix[4]arene-Based Dual Boron–Dipyrrin System.

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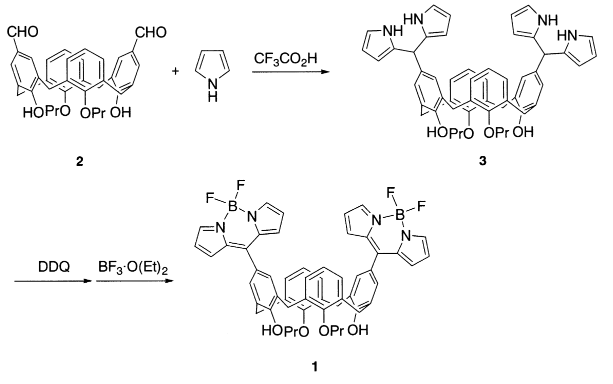
The preparation of a calix[4]arene-based dual boron–dipyrrin system was accomplished by the condensation of diformylcalix[4]arene and pyrrole followed by a treatment with DDQ and diethyl ether–boron trifluoride (1/1). An X-ray crystal structure analysis and spectroscopic measurements revealed that the *cone* conformation of calix[4]arene serves to define 14.9 Å as the center-to-center boron–dipyrrin separation.

Recently, calixarenes[1] and porphyrins[2] have been receiving increasing attention in the field of supramolecular chemistry. To combine the advantages of calixarene and porphyrin, calixarene-porphyrin systems have been synthesized as anion sensors[3] and photoinduced electron transfer models.[4] On the other hand, boron-dipyrrin dye is considered to be an analog of porphyrin, and is frequently used not only as a fluorescent probe for proton or metal detection[5] and as a laser dye, but also in a light-harvesting complex within artificial photosynthetic arrays combined with porphyrins.[6] In this paper, we described the synthesis of a novel bis(boron-dipyrrin) calix[4]arene derivative and its characterization by X-ray crystallography and spectroscopic methods.

A synthetic route to the calix[4]arene derivatives bearing boron-bipyrrin is shown in Scheme 1. Recrystallization from chloroform and hexane afforded yellow crystals of **1**·($CHCl_3$)(C_6H_{14}). An X-ray crystallographic study revealed that a calix[4]arene is fixed as a *cone* conformation. The relatively large R was mainly due to disordering of the solvents. Two propoxy groups had a large thermal factor (B_{eq}), which suggested their high flexibilities. Two boron atoms take a tetrahedral coordination geometry with two nitrogen atoms of dipyrrin and two fluoride atoms. Dipyrrin is an almost planer structure, with the dihedral angle between phenyl rings of calix[4]arene being about 40° (corresponding torsion angles of C2–C1–C29–C30 and C16–C17–C38–C46 are −37(1) and 43(1)°, respectively). The distance between two boron complexes is 14.9 Å (B1 to B2) through space and 17.3 Å through the bond (C29 to C38, 12 bonds). These distances suggest that two complexes on compound **1** are separated so as not to allow an intramolecular interaction between them.



Scheme 1.

The structure of **1** was ascertained from an elemental analysis as well as spectroscopic data. The ^{1}H NMR spectrum of **1** was measured in $CDCl_3$. The whole spectrum shows the pattern expected for **1** with C_{2v} symmetry, and indicates that the boron complexes rotate or twist freely around the C–C bond between calix[4]arene in a solution. The methylene protons between two benzene moieties were observed as being AX type, which is typically observed for calix[4]arene with a *cone* conformation.[7] The absorption and fluorescence spectra of **1** were also measured in CH_2Cl_2. A strong absorption band was observed at 496 nm (ε = 120,000). The extinction coefficient is almost twice as large as that for mono(boron-dipyrrin) compounds, and much larger than that for the Q band of tetraphenylporphyrin (ε = 23,000).[8] The steady-state fluorescence spectrum was also identical for other boron-dipyrrin complexes. Interestingly, the fluorescence yield of **1** was approximately ten-times larger than that of the Zn(II) complex of tetraphenylporphyrin. This indicates that the dual boron-dipyrrin unit would be suitable to funnel energy as an artificial light-harvesting antenna system. All of the results obtained by spectroscopic measurements are in harmony with the solid state structure obtained by X-ray crystallography. In any event, a calix[4]arene-based dual boron–dipyrrin system **1** was synthesized as a precursor to a new pigment for a light-harvesting system by introducing two boron-dipyrrin chromophores for the first time.

Experimental

Diformylcalix[4]arene **2** was prepared according to the literature.[9]

Synthesis of 5,17-Bis(di-2-pyrrolylmethyl)-26,28-dihydroxy-25,27-dipropoxycalix[4]arene (3). To a stirred solution of 1.0 g (1.8 mmol) of **2** in 14 g (0.21 mol) of pyrrole was added a catalytic amount of trifluoroacetic acid, and the solution was stirred for 30 min at room temperature. Purification by silica-gel column chromatography using dichloromethane–ethyl acetate–triethylamine gave 1.2 g (85%) of **3**: pale yellow prisms; mp 154–157 °C; ^{1}H NMR ($CDCl_3$) δ 1.32 (6H, t, J = 7.4 Hz, $OCH_2CH_2CH_3$), 2.02–2.09 (4H, m, $OCH_2CH_2CH_3$), 3.31, 4.28 (each 4H, d, J = 13.2 Hz, Ar-CH_2-Ar), 3.95 (4H, t, J = 6.0 Hz, $OCH_2CH_2CH_3$), 5.34 (2H, s, Ar-CH-(pyrrole)$_2$), 5.94 (4H, bs, pyrrole-H), 6.16 (4H, dd, J = 2.4, 5.8 Hz, pyrrole-H), 6.66 (4H, d, J = 2.4 Hz, pyrrole-H), 6.73 (2H, t, J = 7.3 Hz, Ar), 6.86 (4H, d, J

= 7.3 Hz, *Ar*), 6.88 (4H, s, *Ar*), 7.87 (4H, bs, pyrrole-N*H*), 8.52 (2H, s, O*H*); MS (FAB) *m*/*z* 797 (M^+); Elemental analysis, Found: C, 76.77; H, 6.68; N, 6.56%. Calcd for $C_{52}H_{52}N_4O_4 \cdot H_2O$: C, 76.63; H, 6.68; N, 6.87%.

Synthesis of Bis(boron-dipyrrin) Calix[4]arene (1). To a stirred solution of 1.0 g (1.3 mmol) of **3** in 30 mL of dried toluene was added 0.57 g (1.3 mmol) of DDQ, and the solution was stirred for 15 min at room temperature. Then, 2.5 mL (18 mmol) of triethylamine was added to that solution, followed immediately by boron trifluoride diethyl etherate ($Et_2O \cdot BF_3$, 2.2 mL, 18 mmol). After 45 min, the reaction mixture was purified by silica-gel column chromatography using CH_2Cl_2 to afford 590 mg (52%) of **1**: orange powder; mp > 300 °C; ^{1}H NMR ($CDCl_3$) δ 1.40 (6H, t, J = 7.3 Hz, $OCH_2CH_2CH_3$), 2.10–2.17 (4H, m, $OCH_2CH_2CH_3$), 3.52, 4.40 (each 4H, d, J = 13.2 Hz, Ar-C*H*$_2$-Ar), 4.06 (4H, t, J = 6.0 Hz, $OCH_2CH_2CH_3$), 6.56 (4H, dd, J = 2.5, 4.1 Hz, pyrrole-*H*), 6.93 (2H, t, J = 7.5 Hz, *Ar*), 6.99 (4H, d, J = 2.5 Hz, pyrrole-*H*), 7.04 (4H, d, J = 7.5 Hz, *Ar*), 7.40 (4H, s, *Ar*), 7.91 (4H, bs, pyrrole-*H*), 9.23 (2H, s, O*H*); MS (FAB) *m*/*z* 888 (M^+); Absorption spectrum (CH_2Cl_2, λ_{max}) 438 ($\varepsilon = 3.5 \times 10^4$), 478 (sh, 5.8×10^4), 497 nm (1.2×10^5); Emission spectrum (CH_2Cl_2, λ_{max}) 514 nm; Elemental analysis, Found: C, 69.13; H, 5.12; N, 5.83%. Calcd for $C_{52}H_{46}B_2F_4N_4O_4 \cdot H_2O$: C, 68.89; H, 5.34; N, 6.18%.

Crystal Structure Determination of 1. Single crystals of **1** were recrystallised from a mixture of chloroform and hexane. A yellow prismatic crystal of $\mathbf{1} \cdot (CHCl_3)(C_6H_{14})$ having approximate dimensions of $0.20 \times 0.05 \times 0.05$ mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC7R diffractometer with graphite-monochromated Cu-$K\alpha$. Crystal data. $C_{59}H_{61}B_2Cl_3F_4N_4O_4$, M = 1094.13, orthorhombic, a = 24.184(8), b = 23.463(4), c = 20.085(4) Å, V = 11396(7) Å^3, T = 296 K, space group *Pbca* (No. 61), Z = 8, μ (Cu$K\alpha$) = 19.70 cm^{-1}, 9235 reflections measured, 3100 observed reflections ($|F_0| \geqq 3\sigma\, |F_0|$) used for for the refinement on F. The final R was 0.096 (R_w = 0.126, $w = 1/\sigma^2\,(F_0)$). The program used to solve the structure was SIR92,[10] and that to refine the structure was TEXAN (Fig. 1).[11] The X-ray analysis data have been deposited as Document No. 74060 at the Office of Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; copies can be obtained upon request, free charge, by quoting the publication citation and deposition number 169882.

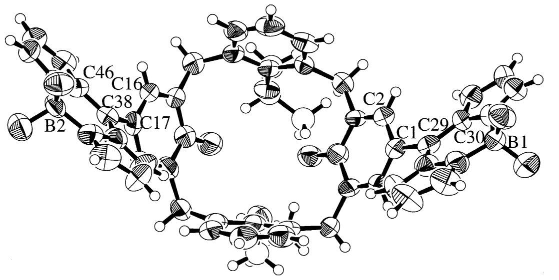


Fig. 1. ORTEP drawing of the structure of **1** (50% probability ellipsoids). For clarity, chloroform and hexane are omitted and propyl groups are shown as spheres of arbitrary radii.

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