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LETTERS

The synthesis and structure of mixed subphthalocyanine/subnaphthalocyanine complexes

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Abstract

The template cyclization of tetrafluorophthalonitrile (A) and 2,3-naphthalenedicarbonitrile (B) with BCl_3 produces two mixed subphthalocyanine/subnaphthalocyanine complexes of the form A_2B and AB_2. Over the series A_3, A_2B, AB_2 and B_3 the Q-band λ_{max} shifts 100 nm: 573 (A_3), 617 (A_2B), 640 (AB_2), 673 nm (B_3). An X-ray crystal structure of the A_2B complex has been determined. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: boron; boron compounds; dyes; macrocycles; X-ray crystal structure.

Subphthalocyanines (SubPcs) are boron-containing macrocycles composed of three isoindoline groups. They have recently attracted attention because of their interesting nonlinear optical properties[1,2] and their use in the formation of unsymmetrical phthalocyanines via the Kobayashi ring-expansion reaction.[3,4] All SubPc syntheses reported to date have utilized a single *ortho*-dinitrile precursor; variations in the physical and optical properties of the macrocycle have been achieved by varying the structure of the dinitrile. We report here the first example of a mixed cyclization using two different *ortho*-dinitrile precursors. By reacting two different dinitriles, A and B, we obtain the two mixed cyclization products A_2B and AB_2, in addition to the unmixed products A_3 and B_3. We find that, in general, the spectral properties of A_2B and AB_2 are intermediate to those of the unmixed macrocycles; this permits the tuning of both the Soret and Q-band energies in a predictable manner. Mixed cyclizations have been used by Barrett, Hoffman and co-workers in the synthesis of the *solitaire-* and *cis/trans gemini*-porphyrazines[5] and by Lindsey et al.[6] in the synthesis of asymmetric porphyrins.

One equivalent of tetrafluorophthalonitrile and 2 equivalents of 2,3-naphthalenedicarbonitrile[7] were heated with 1.5 equivalents of BCl_3 in 1,2,4-trichlorobenzene:1-methylnaphthalene (4:1) for 30 min. The peripheral chlorination that has been reported in other subphthalocyanine reactions[8] was minimized by keeping the reaction temperature under 130°C. The inclusion of 1-methylnaphthalene also appeared to reduce chlorination, presumably by scavenging chlorinating species. Removal of the solvent under

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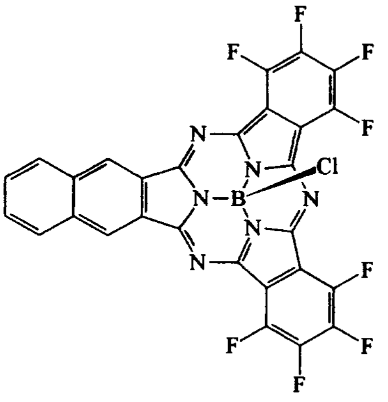
vacuum resulted in the formation of a solid dark blue mass that was dissolved in CH_2Cl_2 and vacuum filtered through a short silica plug to remove polymeric materials. Unreacted starting material was removed by vacuum sublimation at 60°C and 0.1 torr. The crude mixed products, 1[9] and 2,[10] were eluted on a silica column with THF/*n*-hexane (1:2) (R_f=0.70 and 0.50, respectively). Each fraction was shown to consist of a single component by thin layer chromatography. Under the conditions described, 1 and 2 were produced in approximately equal quantities in 20% overall yield (based on tetrafluorophthalonitrile). Only small amounts of the unmixed macrocycles, dodecafluorosubphthalocyanine[11] and subnaphthalocyanine, were formed.



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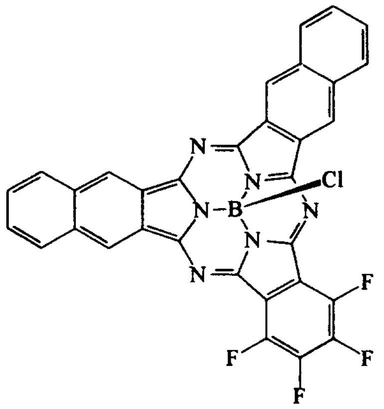

2

Compounds 1 and 2 are readily differentiated by ^{1}H NMR spectroscopy. Both molecules have C_s symmetry and have a single mirror plane that includes the B–Cl bond. This plane bisects the naphthalene group of 1 and renders the hydrogen atoms in the 1 and 4 positions chemically equivalent, resulting in a singlet at 9.43 ppm. Hydrogen atoms 5,8 and 6,7 appear as a pair of four line signals centered at 8.38 and 7.85 ppm, respectively. The mirror plane bisects the tetrafluorophenyl group of 2 and the 1 and 4 hydrogen atoms of the two naphthalene groups are chemically inequivalent. Two peaks are seen at 9.42 and 9.40 ppm. The remaining hydrogen atoms give rise to multiplets at 8.36 and 7.81 ppm.

The electronic absorption spectrum of the perfluorinated SubPc, derived from tetrafluorophthalonitrile, shows a Q-band λ_{max} at 570 nm (ε=60000 M^{-1} cm^{-1})[11] with shoulders of diminishing intensity at 555, 530 and 495 nm. The more extended conjugation of 1, in which one of the tetrafluorophenyl groups has been replaced with naphthalene, results in a red-shift of the lowest energy Q-band absorption to 617 nm (59000 M^{-1} cm^{-1}). High energy features appear as well-resolved maxima at 584 and 525 nm with shoulders at 560 and 495 nm, as shown in Fig. 1. The red-shift continues with the introduction of a second naphthalene unit in 2. Maxima are observed at 640 (69000), 605 and 547 nm and shoulders at 580 and 510 nm. The Q-band λ_{max} for subnaphthalocyanine is 673 nm. The Soret bands of 1 and 2 are at 300 and 319 nm, respectively.

Crystals of 1 suitable for X-ray diffraction were produced as the 1-methylnaphthalene solvate $1\cdot 2(C_{11}H_{10})$ (Fig. 2).[12] The molecule displays the cone shape characteristic of the SubPcs, with approximately tetrahedral geometry about the boron atom. B–N bond distances range from 1.455(5) to 1.490(5) Å; the B–Cl bond distance is 1.875(4) Å. Average values for the N–B–N and N–B–Cl bond angles are 105.3(3)° and 113.4(3)°, respectively. Disordered 1-methylnaphthalene molecules give rise to the somewhat high *R* values.[13]

Studies of the electrochemical, luminescent and nonlinear optical properties of these new complexes are in progress.

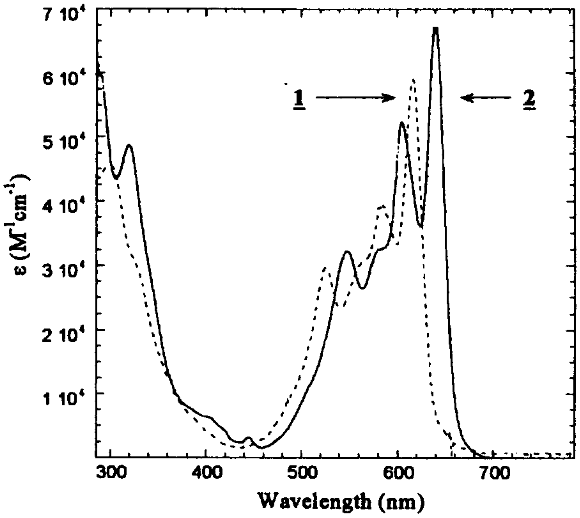

Figure 1. Electronic spectra of 1 (- - -) and 2 (—) in CH_2Cl_2

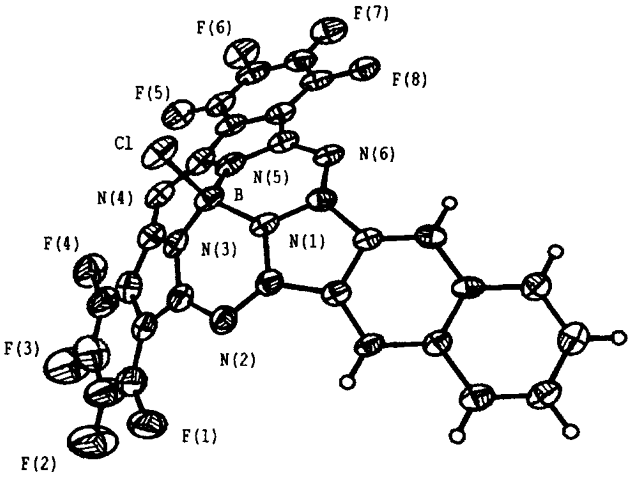

Figure 2. Thermal ellipsoid plot of 1

Acknowledgements

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9. Compound **1**: mp=305–310°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85 (m, 2H), 8.38 (m, 2H), 9.43 (s, 2H); UV–vis: λ_{max}=617 nm (ε=59 000 M^{-1} cm^{-1}), 584 (40 000), 560 (sh), 525 (30 000), 495 (sh), 300 (46 000); HRMS (FAB) M^+=624.0314 (calcd for $C_{28}H_6BClF_8N_6$: 624.0308). Mass spectra were obtained at the Michigan State University Mass Spectrometry Facility, which is supported in part by a grant (DRR-00480) from the Biotechnology Research Technology Program National Center for Research Resources, National Institute of Health.
10. Compound **2**: mp >340°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81 (m, 2H), 8.36 (m, 2H), 9.40 (s, 1H), 9.42 (s, 1H); UV–vis: λ_{max}=640 nm (ε=69 000 M^{-1} cm^{-1}), 605 (51 000), 580 (sh), 547 (34 000), 510 (sh), 319 (54 000); HRMS (FAB) M^+=602.0866 (calcd for $C_{32}H_{12}BClF_4N_6$: 602.0841).
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12. X-Ray crystallographic data for $\mathbf{1}\cdot 2(C_{11}H_{10})$: $C_{50}H_{26}BClF_8N_6$, M=909.05, space group: P2/n (no. 13), a=20.9556(6) Å, b=7.8004(2) Å, c=26.5274(8) Å, β=112.7160(10)°, V=3999.9(2) Å^3, Z=4, plate, purple, 0.30×0.11×0.04 mm, Mo$K\alpha$, λ=0.71073 Å, 7392 reflections, 4329 with $I>2.00\sigma(I)$, T=136 K, R=8.0%, R_w=21.9%, GOF=1.075. $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, $R_w=[\Sigma\{w(F_o^2-F_c^2)^2\}/\Sigma\{wF_o^2\}^2]^{1/2}$ and $GOF=[\Sigma\{w(F_o^2-F_c^2)^2\}/(M-N)]^{1/2}$, where M=number of reflections and N=number of parameters refined.
13. Two molecules of 1-methylnapthalene were located in the asymmetric unit. These were grossly disordered and the electron density and void space were analyzed using PLATON and SQUEEZE (Spek, 1998, Univ. Utrecht, Utrecht, The Netherlands). Analysis confirmed the 1-methylnapthalene model. SQUEEZE generated a new Fobs file after subtracting contributions from these regions of disordered electron density. The model fit improved by 50%.