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Tribenzosubporphines: Synthesis and Characterization**

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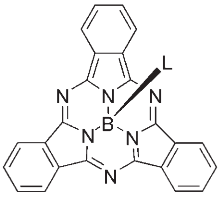
Subphthalocyanines **1** possess a unique position in the chemistry of phthalocyanines as a ring-contracted congener of phthalocyanine. Since the first synthesis of subphthalocyanines by Meller and Ossko in 1972,[1] they have continued to gather much interest in light of their 14π-electron aromatic circuit, triangular bowl-shaped structures, intense fluorescence, and nonlinear optical properties.[2] In sharp contrast, subporphyrin, which is a porphyrinic counterpart of **1**, remains a missing player, thus leaving its study totally untouched, despite recent extensive reports of various ring-expanded and ring-contracted porphyrins.[3] Subporphyrins are expected to be promising macrocycles from both basic and



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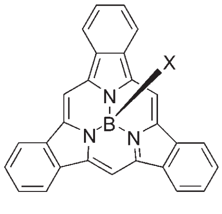
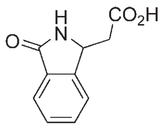


2a (X = OH)
2b (X = OMe)
2c (X = O*i*Pr)



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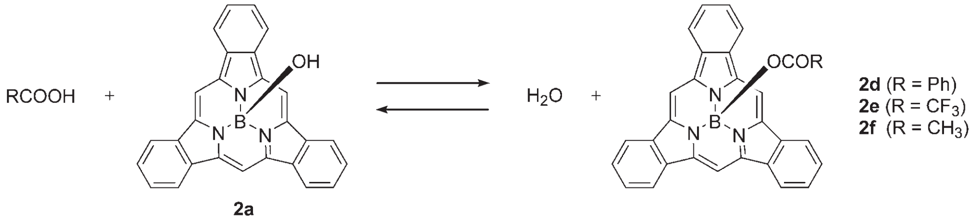
applied viewpoints, as judged from the various interesting attributes of subphthalocyanines.[2] Thus, a reliable synthetic route to subporphyrins is highly desirable. Herein we report the synthesis and characterizations of [14]tribenzosubporphine(1.1.1)boron(III) complexes **2a**–**f**. To the best of our knowledge, this is the first report on the synthesis of subporphyrins.

The hydroxyboron complex of tribenzosubporphine **2a** was synthesized by a modified protocol developed by Gouterman and co-workers[4] for the synthesis of a tetrabenzoporphine using 2-(3-oxo-2,3-dihydro-1*H*-isoindol-1-yl)acetic acid (**3**) and with replacement of the template from a Zn^{II} to a B^{III} ion.[1,2] Compound **3** and boric acid were mixed, ground into a fine powder, and subsequently heated to 350 °C in an N_2 atmosphere for 3.5 h. TLC analysis of the resulting black melt indicated formation of many products, from which a fraction eluting at $R_f = 0.30$ on a silica gel TLC plate with a 1:2:2 mixture of diethyl ether/hexane/dichloromethane was isolated. This product was identified as **2a** on the basis of its parent ion signal by MALDI-TOF mass analysis and its characteristic strong green fluorescence. Repeated separations by chromatography on silica gel gave **2a** as an orange solid in 1.4 % yield. Phenylboronic acid or 4-methoxyphenylboronic acid can also be used as the template and give **2a** in comparable yields. The subporphyrin **2a** can also be prepared in 1.2 % yield under irradiation with a domestic microwave oven (output: 500 W) for 30 minutes. Although the yields are low, the syntheses of **2a** is quite reproducible.

Reflecting its C_3 symmetry, the subporphyrin **2a** exhibits a very simple ^{1}H NMR spectrum that consists of a singlet at $\delta = 9.44$ ppm for the *meso* positions, a pair of double doublets for the benzo protons at $\delta = 8.86$ and 7.88 ppm, and a signal at $\delta = -2.60$ ppm for the hydroxy proton. The observed chemical shifts indicate a diatropic ring current in line with its 14π-electronic network. The ^{13}C NMR spectrum also supports the structure of **2a**, with signals observed at $\delta = 137.0$ and 131.6 ppm for the pyrrolic carbon atoms, signals at $\delta = 127.2$ and 121.5 ppm for the fused benzo carbon atoms, and a signal at $\delta = 97.3$ ppm for the *meso* carbon atom. The ^{11}B NMR spectrum exhibits a singlet at $\delta = -14.6$ ppm, which is slightly less shielded relative to those of subphthalocyanines which appear in the range of $\delta = -17.7$ to -19.6 ppm.[2a] The high resolution electrospray ionization time-of-flight (HRESI-TOF) mass spectrum of **2a** also supports the structure, with a signal at *m*/*z* 409.1387 (calcd for $[C_{27}H_{16}BN_3O]^+$: *m*/*z* 409.1386). The structure of **2a** has been confirmed by X-ray diffraction analysis to be a bowl-shaped tribenzosubporphine structure (Figure 1 a).[5]



Scheme 1. Equilibria between **2a** and **2d**–**f**.

A solution of **2a** in diethyl ether was stirred in the presence of $H_2{}^{18}O$ for 6 h at room temperature. ESI-TOF mass analysis of this reaction mixture detected two main signals at *m*/*z* 409.14 and 411.14, thus suggesting a facile replacement of the axial hydroxy group. A similar exchange reaction has also been observed on dissolving **2a** in methanol, which immediately gave rise to the appearance of a new spot of **2b** on the TLC plate which became the single product upon refluxing the solution. The methoxy protons of **2b** are observed at $\delta = 0.81$ ppm in the ^{1}H NMR spectrum because of the diatropic ring current. Similarly, refluxing **2a** in 2-propanol afforded isopropoxyboron complex **2c**, which gives rise to signals corresponding to the isopropoxy protons at $\delta = 0.63$ (1 H) and -0.42 ppm (6 H) in the ^{1}H NMR spectrum. The subporphyrin **2c** is easily hydrolyzed to **2a** by a small amount of adventitious water in solution, while **2b** is rather stable under basic or neutral conditions, but is readily hydrolyzed in acidic aqueous solution.

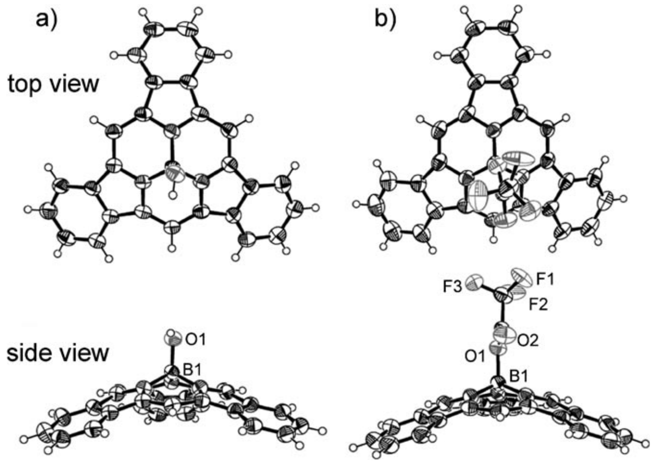


Figure 1. Crystal structures of a) **2a** and b) **2e** at 50 % probability of thermal ellipsoids.

The axial hydroxy group of **2a** can be also exchanged by a carboxy group by stirring it in the presence of an excess amount of carboxylic acid, thus providing **2d**, **2e**, and **2f** through the equilibrium shown in Scheme 1. The equilibrium between **2a** and **2d** could be easily followed by ^{1}H NMR spectroscopy and allowed for the determination of an equilibrium constant of 3.2 (Supporting Information). Stirring a solution of **2a** in the presence of an excess amount of carboxylic acid or continuous removal of water from the reaction mixture gave the carboxyboron complexes in high yields. The ^{11}B NMR spectra of **2d**–**f** exhibit characteristic, extremely broad signals in the range of $\delta = -13.7$ to -14.6 ppm, and contrast the relatively sharp signals of the hydroxy- and alkoxyboron complexes **2a**–**c**.

Furthermore, X-ray diffraction analysis shows that in the solid-state the macrocycles **2b**, **2c**, and **2e** have bowl-shaped structures, with a variable curvature that depends on the axial group (see Figure 1b and the Supporting Information).[5] The degree of curvature can be characterized by the depth of the bowl, which is defined as the distance from the lowest edge of the macrocycle (the mean plane of the peripheral six carbon atoms of the benzene rings) to the boron atom and is 2.33 Å for **2a**, 1.70 Å for **2b**, 2.10 Å for **2c**, and 2.02 Å for **2e**. The bowl depths of the subporphyrins are less than that (2.55 Å) of subphthalocyanine **1** (L = OH),[2c] and **2b** is the shallowest bowl in the series.[6] The average N-B-N angles are 105.1° for **2a**, 105.5° for **2b**, 105.2° for **2c**, and 108.4° for **2e**, and the average B−N bond lengths are 1.51 Å for **2a**, 1.50 Å for **2b**, 1.51 Å for **2c**, and 1.48 Å for **2e**, and the B−O bond lengths are 1.446(4) Å for **2a**, 1.445(5) Å for **2b**, 1.435(3) Å for **2c**, and 1.506(5) Å for **2e**, respectively. These structural parameters suggest **2e** has a different electronic nature from those of **2a–c**. A possible explanation may be that the B−O bond for **2e** has a larger ionic character than those of **2a–c**. Overall the bowl-shaped structures of the subporphyrins are similar to those of subphthalocyanines.[7]

The absorption spectrum of **2a** exhibits a sharp Soret band at 355 nm with a shoulder at 337 nm, and Q bands at 480 and 514 nm, which are blue-shifted relative to those of metalloporphyrins mainly because of the reduced π-conjugation pathway (Figure 2). The Q bands show a vibronic structure similar to those of subphthalocyanines and benzoporphyrins with large molar extinctions of the Q band of $9\times10^4\,\text{M}^{-1}\,\text{cm}^{-1}$, which is more than three times larger than the value ($2.97\times10^4\,\text{M}^{-1}\,\text{cm}^{-1}$) of Zn$^{\text{II}}$TPP (TPP = tetraphenylporphyrin). The strong and sharp Soret bands with an extinction coefficient of $1.64\times10^5\,\text{M}^{-1}\,\text{cm}^{-1}$ differ significantly from the rather broad Soret bands of subphthalocyanines around 300 nm and are similar to the Soret bands of porphyrins. This similarity has been confirmed by calculation of the molecular orbitals (MOs) at the B3LYP/6-31G* level (see the Supporting Information). The π–π* transitions calculated by time-dependent density functional theory (TD-DFT) match well with the absorption spectrum of **2a** (indicated by vertical bars in Figure 2).[8] Interestingly, **2a** exhibits intense green fluorescence at 517 nm with $\Phi_F = 0.41$,[9] whose decay has been found to obey a single exponential function with $\tau = 3.4 \pm 0.2$ ns, as determined by the time-correlated single-photon counting technique. The lowest triplet excited state (T_1) of **2a** has been detected in CH_2Cl_2 by nanosecond time-resolved transient absorption spectroscopy to have a broad absorbance in the range 350–700 nm whose decay follows a single exponential function with $\tau = 54$ μs. Furthermore, femtosecond time-resolved transient absorption anisotropy measurements revealed that the anisotropy value is initially about 0.12 and decays with $\tau = 46 \pm 0.5$ ps. This decay has been assigned to its rotational diffusion time which is distinctly shorter than that (130 ps) of Zn$^{\text{II}}$TPP,[10] thus reflecting the smaller molecular size of **2a** compared with that of Zn$^{\text{II}}$TPP. Overall, the optical properties of the 14π-electron conjugated aromatic subporphyrins can be regarded as analogous to those of 18π-electron conjugated porphyrins, despite differences that reflect the structural difference in the molecular symmetry and molecular size.

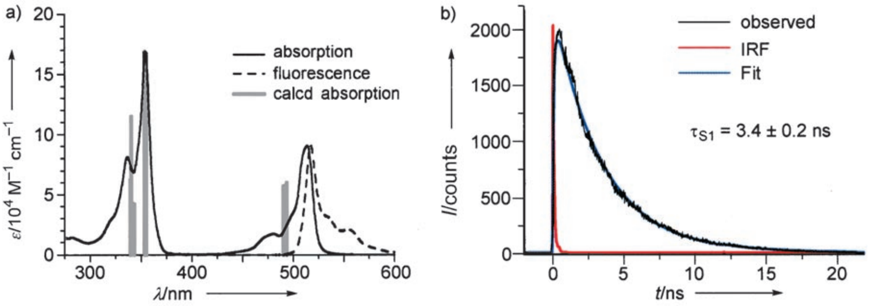


Figure 2. a) Absorption and fluorescence spectra of **2a** in CH_2Cl_2, and calculated absorption bands, and b) the fluorescence decay of **2a**.

The electrochemical properties of **2a** and **2b** in acetonitrile have been examined by cyclic voltammetry using tetraethylammonium perchlorate as a supporting electrolyte. The first and second one-electron oxidation potentials were determined to be 0.30 and 0.92 V and 0.31 and 0.93 V, as reversible and irreversible waves, versus the ferrocene/ferrocenium ion couple for **2a** and **2b**, respectively, while the reduction-associated waves could not be detected up to −2.0 V. Thus, it may be concluded that subporphyrins are better electron donors than subphthalocyanines.[2a,11]

In summary, the first synthesis of tribenzosubporphyrin **2** has been achieved through the one-pot condensation of **3** in the presence of boric acid as a template. Detailed comparative studies of the optical and electrochemical properties of **2** with those of porphyrins, phthalocyanines, and subphthalocyanines will generate a deeper understanding of the electronic nature of porphyrins and phthalocyanines, and possible applications of **2** to dye-based devices will be worthy of further investigations.

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[5] Crystallographic data for **2a**: $C_{27}H_{16}BN_3O \cdot H_2O$, $M_r = 409.24$, monoclinic, space group $C2/c$ (no. 15), $a = 24.535(5)$, $b = 11.708(3)$, $c = 13.940(3)$ Å, $\beta = 91.192(14)°$, $V = 4003.5(15)$ Å^3, $T = 123$ K, $\rho_{calcd} = 1.358\ g\,cm^{-3}$, $Z = 8$; $R_1 = 0.0681$ ($I > 2\sigma(I)$), $R_w = 0.2176$ (all data), GOF = 1.181. Crystallographic data for **2b**: $C_{28}H_{18}BN_3O$, $M_r = 423.26$, orthorhombic, space group P_{nma} (no. 62), $a = 16.272(2)$, $b = 17.852(2)$, $c = 6.8503(9)$ Å, $V = 1990.0(4)$ Å^3, $T = 90$ K, $\rho_{calcd} = 1.413\ g\,cm^{-3}$, $Z = 4$; $R_1 = 0.0947$ ($I > 2\sigma(I)$), $R_w = 0.1970$ (all data), GOF = 1.335. Crystallographic data for **2c**: $C_{30}H_{22}BN_3O$, $M_r = 451.32$, monoclinic, space group $P2_1/c$ (no. 14), $a = 9.8657(11)$, $b = 13.8409(15)$, $c = 17.1556(18)$ Å, $\beta = 104.831(7)°$, $V = 2264.6(4)$ Å^3, $T = 123$ K, $\rho_{calcd} = 1.324\ g\,cm^{-3}$, $Z = 4$; $R_1 = 0.0584$ ($I > 2\sigma(I)$), $R_w = 0.1765$ (all data), GOF = 1.005. Crystallographic data for **2e:** $C_{29}H_{15}BN_3O_2F_3$, $M_r = 505.25$, monoclinic, space group $P2_1/n$ (no. 14), $a = 9.5441(11)$, $b = 15.8360(17)$, $c = 15.4303(18)$ Å, $\beta = 102.245(7)°$, $V = 2279.1(4)$ Å^3, $T = 123$ K; $\rho_{calcd} = 1.473\ g\,cm^{-3}$, $Z = 4$; $R_1 = 0.0722$ ($I > 2\sigma(I)$), $R_w = 0.2223$ (all data), GOF = 1.242; CCDC-281754–281757 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[6] Crystal-packing diagrams are pairwise dimeric forms for **2a**, **2c**, and **2e**, whereas J-aggregation-type packing is seen for **2b** (see the Supporting Information). This situation may lead to the shallowest bowl depth in **2b**.

[7] In **1** (L = OH), the average N-B-N angle, B−N bond length, and B−O bond length are reported in Ref. [2c] to be 102.9°, 1.49 Å, and 1.438(14) Å, respectively.

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