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Synthesis and crystal structure of core-modified benziporphyrin: thia-*p*-benziporphyrin

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Abstract—The core-modified 5,20-phenyl-10,15-tolyl-thia-*p*-benziporphyrin (SBzP) can be prepared from the condensation of 1,4-bis(α-hydroxyl-benzyl)benzene with 5,10-ditolyl-16-thia-5,10,15,17-tetrahydrotripyrrin using $BF_3{\cdot}OEt_2$ as catalyst. Spectroscopic studies suggest an aromatic macrocycle with a rapid flipping phenylene ring. SBzP exhibits a tilted phenylene ring and crystal packing shows dimeric structure with two SBzP rings linked by hydrogen bonding and π–π interaction. TFA acidified $SBzPH_2{}^{2+}$ has a saddle-shaped dication porphyrin ring with two solvated trifluoroacetate and two solvated trifluoroacetic acid linked by hydrogen bondings.

Carbaporphyrin is a porphyrinoid with at least one of the nitrogens in the inner porphyrin core replaced with a carbon. The first carbaporphyrin, *N*-confused porphyrin, was reported in 1994 independently by Furuta[1] and Latos-Grazynski.[2] Following with the pioneer works, several *meso*- or β-pyrrole substituted carbaporphyrins have been reported.[3,4] More recently, the core-modified *N*-confused porphyrins with an inner pyrrolic nitrogen replaced by heteroatoms such as oxygen or sulfur have been reported.[5] The *N*-confused tetraphenylporphyrin (NCTPP), which has an inverted pyrrole ring linked to the *meso* carbons through one α and one β-pyrrolic carbon, is the most studied carbaporphyrin. Recent reports demonstrated that NCTPP exhibits distinct physical properties and unusual chemistry comparing to a regular porphyrin. For examples, rich tautomeric forms[6] and a unique ring fusion reaction to form an internal tricyclic ring[7] were reported. Importantly, the *N*-confused porphyrin, which has an CH in the inner coordination sphere, provides a template for the formation of an organometallic metal–carbon bond and was found to be able to stabilize unusual metal oxidation states.[8] NCTPP coordinates to Fe(II) through an unusual tridentate chelating fashion with inverted pyrrole ring tilted away from mean porphyrin plane.[9] The oxidation of Fe(II) to Fe(III), accompanying with an activation of inner C–H bond, forms a direct organometallic iron–carbon bond.[10]

Similar to *N*-confused porphyrins, benziporphyrin, a porphyrinoid with a pyrrole ring replaced by a benzene ring, provides a good template for the study of organometallic reaction within porphyrin systems. Comparing with the progresses on NCTPP, the chemistry of benzi-type carbaporphyrin is not much explored. The syntheses of *meta*- and *para*-benziporphyrin[11,12] have been reported recently and the cadmium complex of *p*-benziporphyrin has been structurally characterized. Not until recently Chandrashekar and co-workers[13] reported the core-modified oxybenziporphyrin and its Pd complex. There is still no real thia-*p*-benziporphyrin type compound available in the literature. As an effort to expand the groups of carbaporphyrin, here we report the synthesis, characterization, and crystal structure of a novel core modified thia-*p*-benziporphyrin.

Synthesis of 5,20-phenyl-10,15-tolyl-thia-*p*-benziporphyrin is demonstrated in Scheme 1. The condensation of thiophene with tolylaldehyde gave 2,5-bis(tolylhydroxylmethyl)thiophene. This diol was treated with excess pyrrole to obtain the starting tripyrrin, 5,10-ditolyl-16-thia-5,10,15,17-tetrahydrotripyrrin.[14] The '3+1' condensation of tripyrrin with 1,4-bis(α-hydroxylbenzyl)benzene in CH_2Cl_2 using $BF_3{\cdot}OEt_2$ as acid catalyst following with a DDQ oxidation afforded

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Keywords: porphyrinoid; benziporphyrin; carbaporphyrin.

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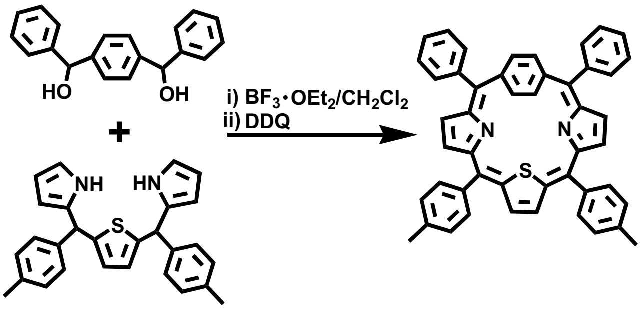

Scheme 1.

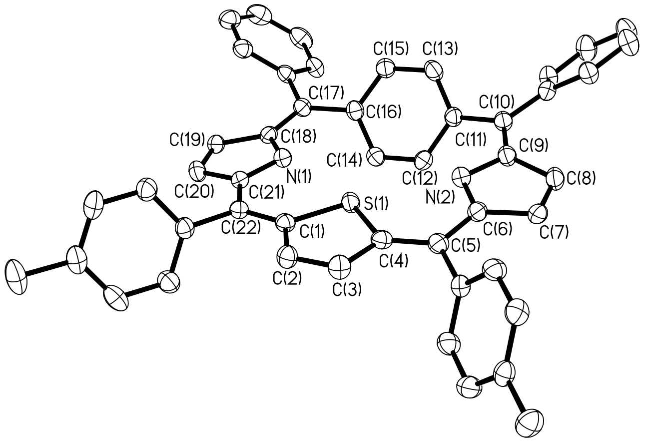

Figure 2. The thermal ellipsoid plot of SBzP in 50% ellipsoid.

thia-*p*-benziporphyrin in 6% yield.[15] The usage of TFA as acid catalyst for the condensation reaction gives no detectable thia-*p*-benziporphyrin on TLC. The porphyrinato characteristic of thia-*p*-benziporphyrin is demonstrated by UV–vis spectrum shown in Figure 1, where a Soret type absorption band appears at $\lambda_{max} = 440$ nm ($\log \varepsilon = 4.92$) and a *Q* band appears at 592 nm ($\log \varepsilon = 4.59$). The UV–vis pattern of SBzP resembles *p*-benziporphyrin with the Soret band slightly red-shifted.[12]

The NMR spectrum of thia-*p*-benziporphyrin at 293 K agrees with an aromatic macrocycle exhibiting largely C_{2v} symmetry. The β-thiophenic proton resonates as sharp singlet at 8.20 ppm, while two doublets at 8.10 and 7.58 ppm were assigned as β-pyrrolic protons. The sharp singlet at 5.54 ppm integrated into four protons was assigned as the phenylene protons. This peak broadens into a peak with half-width of 42 Hz at 233 K. This result is consistent with a rapid flipping of *p*-phenylene ring at room temperature but slows down when the temperature decreased. A similar phenomenon has been observed in the NMR spectra of benziporphyrins.[12]

The crystal structure of SBzP is depicted in Figure 2.[16] The structure showed a comparable conformation to TPBP with a relatively flat macrocycle except the tilt phenylene ring. The averaged deviation of 19 atoms from the mean plane defined by two pyrrole rings, one thiophene ring, and four *meso* carbons is 0.1141 Å. The tilting angle between the phenylene ring and the mean 19-atom plane is 48°. This value is identical to the corresponding angle in tetraphenyl-*p*-benziporphyrin (TPBP).[12] The dihedral angles between *meso* substituents and mean 19-atom plane categorize into two groups with distinct values. The phenyl rings neighboring to porphyrinato phenylene group have dihedral angles of 33° and 36°, which are much smaller than 60° and 67° for the tolyl ring on the tripyrrin unit. In addition, the bond lengths of 1.473(3) and 1.476(3) Å between *meso* carbons and the phenyl rings are significantly shorter than 1.502(3) and 1.499(3) Å between *meso* carbons and the tolyl rings. The smaller dihedral angles along with the shorter bond lengths suggest a minor degree of aromatic delocalization between the *meso* phenyl rings and the porphyrin conjugate system. The bond length of 1.378(3) for C13–C15 and 1.362(3) for C12–C14 are shorter than other bond lengths on phenylene ring and suggests the contribution of the quinoid tautomer form as suggested by Latos-Grazynski in the structure of TPBP.[12] As shown in Figure 3, in the crystal lattice, SBzP forms a dimeric structure with mutual overlaying of pyrrole rings with thiophene rings on the counterpart of SBzPs. Hydrogen bonding interactions from H25 on a carbon of tolyl ring to a pyrrolic nitrogen with distance of 2.528 Å link two SBzP rings and the average separation between the overlapping regions is 3.7192 Å, which is within the distance for π–π interaction between two porphyrins.[17]

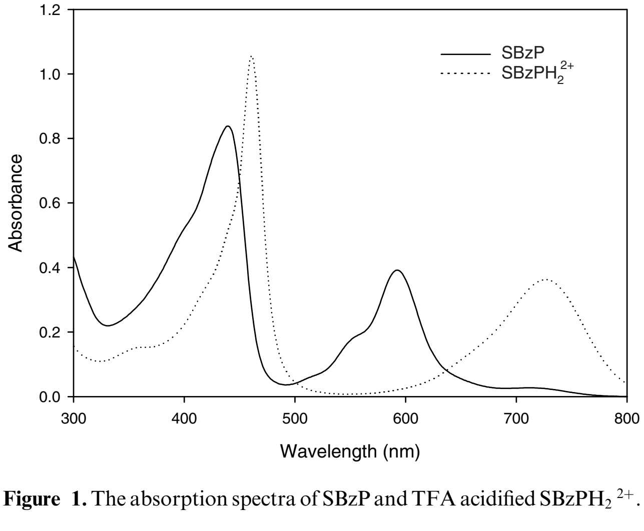

Figure 1. The absorption spectra of SBzP and TFA acidified SBzPH$_2$$^{2+}$.

When treated with TFA, the Soret and *Q* bands of SBzPH$_2$$^{2+}$ significantly red-shifted to 461 nm ($\log \varepsilon = 5.02$) and 726 nm ($\log \varepsilon = 4.96$) in agreement with the observation for other protonated porphyrins. The solid state structure obtained from the crystal of acidified solution of SBzPH$_2$$^{2+}$ gave a much distorted porphyrin core (Fig. 4). The averaged deviation of atoms from mean 19-atom plane of pyrrole, thiophene rings, and *meso* carbons is 0.3274 Å. The dihedral angle between phenylene ring and mean 19-atom plane for protonated SBzPH$_2$$^{2+}$ of 53° is slightly larger than the

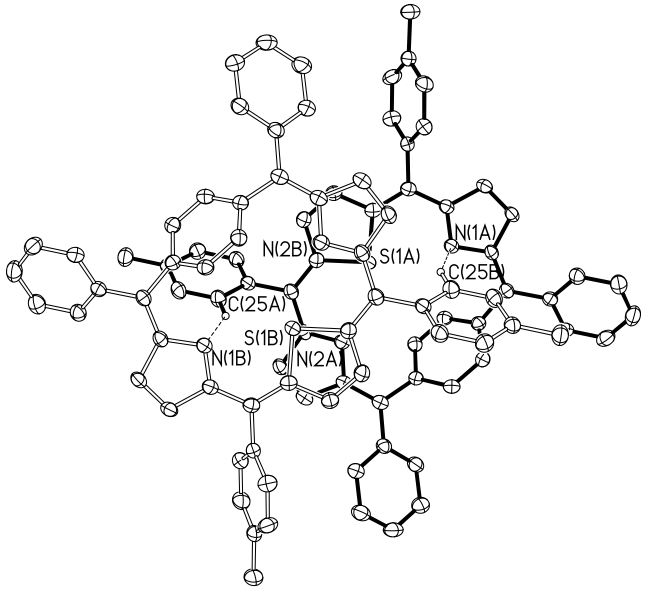

Figure 3. Hydrogen bonding and π–π interaction in the dimeric structure of SBzP.

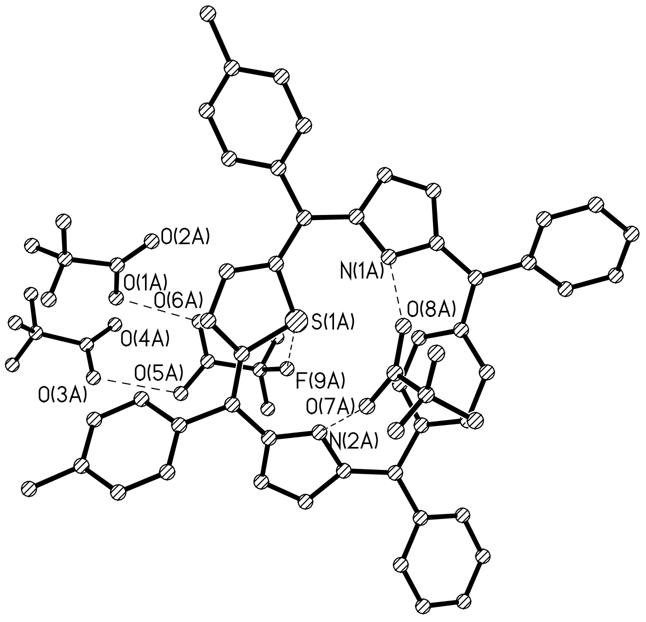

Figure 4. Structure and hydrogen bonding interaction in the solid state structure of dicationic $\mathrm{SBzPH_2}^{2+}$. Selected interatomic distances (Å): O(7A)···N(2A) 2.649, O(8A)···N(1A) 2.624, S(1A)···F(9A) 3.265, O(6A)···O(1A) 2.533, O(5A)···O(3A) 2.541.

corresponding angle on the neutral SBzP. The increasing pyrrolic C–N–C bond angles from 106.90(19) and 107.0(2) to 111.4(4) and 111.1(4) suggest protonation on both pyrrole rings.[18] The analyses of the inter-molecular interactions reveal that a solvated trifluoroacetate rides above the macrocycle with two oxygens of the acetate group hydrogen bonding to pyrrolic N–Hs. A fluorine atom of the second trifluoroacetate closely contacts to sulfur on the thiophene ring with a distance of 3.265 Å. The oxygens of this trifluoroacetate further interact to two solvated trifluoroacetic acids through hydrogen bonding interactions to form a complicated hydrogen bonding network.

In conclusion, we have demonstrated that the thia-*p*-benziporphyrin can be synthesized with reasonable yield. The physical properties suggest that it is an aromatic macrocycle with a flipping phenylene ring. The solid state structure of $\mathrm{SBZPH_2}^{2+}$ shows the binding of an anionic trifluoroacetate above the benziporphyrin ring.

Acknowledgements

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15. General procedure for the preparation of SBzP: 5,10-ditolyl-16-thia-5,10,15,17-tetrahydrotripyrrin (0.211 g, 0.50 mmol) was dissolved in CH_2Cl_2 (150 mL). To this solution, 1,4-bis(α-hydroxyl-benzyl)benzene (0.145 g, 0.50 mmol) was added. The reaction mixture was bubbled with N_2 for 10 min and BF_3·$(OEt)_2$ (50 μL) was then injected. After 2 h DDQ (0.5 g, 2.2 mmol) was added and stirred for another 30 min. After solvent removal the residue was transfered to a column packed with a slurry of aluminum oxide in CH_2Cl_2 and eluted by CH_2Cl_2. After

the elution of dithiaporphyrin, the desired SBzP was eluted out as a green fraction. The eluent of SBzP was collected, dried on a rotovapor and recrystallized from toluene/hexane to afford 22 mg of SBzP (6% yield). UV–vis (CH_2Cl_2): λ_{max} (nm) (log ε): 440 (4.92), 592 (4.59). ^1H NMR ($CDCl_3$, 600 MHz): δ (ppm) = 8.20 (s, 2H, β-thiophene-H), 8.10 (d, 2H, β-pyrrole-H), 8.08 (d, 4H, tolyl-H), 7.69–7.61 (m, 10H, phenyl-H), 7.58 (d, 2H, β-pyrrole-H), 7.40 (d, 4H, tolyl-H), 5.54 (s, 4H, phenylene-H), 2.55 (s, 6H, methyl-H). MS (FAB): $[M+H]^+$ (*m/z*) 761 (Calcd 761.25). HRMS: 761.2520. Anal. Calcd for $C_{48}H_{34}N_2S_1{\cdot}0.35C_6H_{14}$: C, 85.84; H, 5.59; N, 3.99. Found: C, 84.66; H, 5.42; N, 3.76.

16. Crystal structure data was collected on a Bruker Smart 1000 CCD diffractometer at 150 K. SBzP was refined to $R = 0.0557$, $W_R = 0.1268$ for 8286 independent reflections while $SBzPH_2{}^{2+}$ was refined to $R = 0.0613$, $W_R = 0.1317$ for 15,479 independent reflections. Crystallographic data (excluding structure factors) for the structures in this paper, have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 218499 (SBzP) and 218500 ($SBzPH_2{}^{2+}$). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).
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