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Communication

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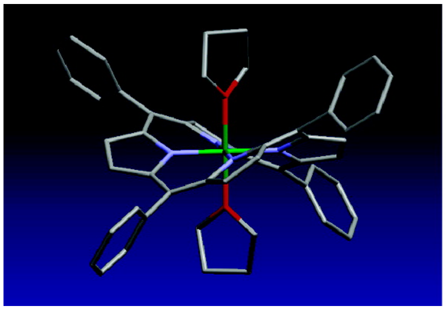

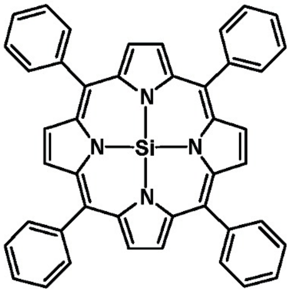

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An Antiaromatic Porphyrin Complex: Tetraphenylporphyrinato(silicon)(L)$_2$ (L = THF or Pyridine)

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We have been investigating highly reducing, neutrally charged molecules as isostructural n-dopants for molecular semiconductors.[1,2] Porphyrin complexes are ideal candidates for the implementation of isostructural doping because the oxidation state of the porphyrin ring can be changed while maintaining charge neutrality of the molecule as a whole by changing the identity of the metal center in the complex. For example, the known monolithium tetraphenylporphyrin complex, Li(TPP)[3], is an oxidized molecule in which the oxidation state of the porphyrin ring is 1−, and the complex, therefore, might be expected to act as a p-dopant for the isostructural Zn(TPP). However, their solution-phase electrochemical redox potentials indicate that Li(TPP) will not spontaneously accept an electron from Zn(TPP).[4] A better candidate would be a porphyrin complex that is two redox steps away from the normal valence of 2− for the porphyrin ring. In the present communication, we report the synthesis of tetraphenylporphyrinato(silicon)(L)$_2$ (Si(TPP)(L)$_2$, L = THF or pyridine), a reduced porphyrin complex in which the oxidation state of the porphyrin ring is best described as 4− and the complex is antiaromatic.

Reduction of Si(TPP)Cl$_2$[5] with 2 equiv of Na/Hg in THF yields air-sensitive, dark red-orange Si(TPP)(THF)$_2$·2THF in 49−59% yield after filtration in THF/toluene and precipitation from THF/hexane. The THF complex can be converted to Si(TPP)(py)$_2$·2py by dissolving it in pyridine, removing the pyridine and THF under vacuum, and then precipitating from pyridine/hexane. Crystals of Si(TPP)(THF)$_2$·2THF suitable for single-crystal X-ray diffraction were grown by performing the reduction of Si(TPP)Cl$_2$ in an unstirred THF solution. An ORTEP representation of the solid-state structure of Si(TPP)(THF)$_2$ is given in Figure 1.

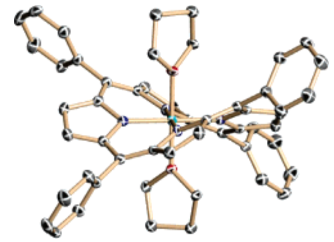

Figure 1. Solid-state structure of Si(TPP)(THF)$_2$.

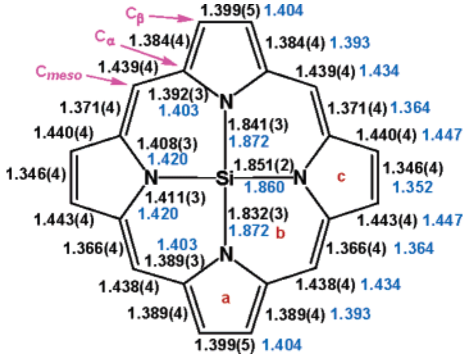

Figure 2. Valence-bond structure of Si(TPP) with bond distances (Å) from the crystal structure of Si(TPP)(THF)$_2$ (black) and calculated (B3LYP/6-31G*) for Si(TMP)(OMe$_2$)$_2$ (blue). C−C distances are outside the ring. C−N and Si−N distances are inside the ring (only crystallographically unique distances are shown). Letters *a*, *b*, and *c* indicate where NICS calculations were performed.

One striking aspect of the structure of Si(TPP)(THF)$_2$ is that it is highly ruffled.[6] The four nitrogen atoms and the silicon are all coplanar, such that the coordination around silicon is almost perfectly octahedral, while the meso carbons (C$_{meso}$; see Figure 2) lie above and below the SiN$_4$ plane. The degree of nonplanarity of a ruffled porphyrin can be gauged by the displacement of the meso carbons from the N$_4$ plane. In Si(TPP)(THF)$_2$, the two pairs of crystallographically equivalent meso carbons are displaced from the N$_4$ plane by 1.003 and 0.996 Å, respectively, indicating a highly ruffled structure. Porphyrin complexes will adopt a ruffled structure for two reasons: bulky meso substituents[7] or an atom with a small covalent radius at the center of the complex,[8] as in Si(TPP)(THF)$_2$ (a ruffled structure leads to shorter M−N bonds). Phosphorus(V) has the smallest covalent radius of any element that has been incorporated into a porphyrin, and its complexes[9,10] are the most severely ruffled: C$_{meso}$ atoms are usually displaced by about 0.8−1.0 Å from the N$_4$ plane. Porphyrin complexes of silicon are also often quite ruffled (C$_{meso}$ displacements of ∼0.6−0.8 Å),[5,11,12] but several are approximately planar.[12,13] The ruffling of silicon porphyrins is generally not as large as in phosphorus porphyrins because silicon has a larger covalent radius than phosphorus.[14] Si(TPP)(THF)$_2$, however, is as ruffled as the most ruffled P(V) porphyrins because the electronic structure of Si(TPP) is different from other porphyrin complexes; the valence-bond structure given in Figure 2 is a good representation of the bonding in Si(TPP). Instead of the usual two covalent bonds and two dative bonds to the central atom, Si(TPP) has four regular covalent bonds between the porphyrin nitrogen atoms and the silicon atom. This is reflected in the Si−N bond lengths of Si(TPP)(THF)$_2$ (see Figure 2), which are shorter than those in any of the previously reported silicon porphyrins, and are comparable to the P−N bond lengths in the most ruffled phosphorus porphyrins.

The most unusual feature evident in the structure of Si(TPP)(THF)$_2$ is the C−C bond length alternation around its periphery (see Figure 2), which is without precedent in crystallographically characterized porphyrin complexes. (Metalloporphyrin π-cation radicals often exhibit bond length alternation along the 16-membered C−N inner ring.[15,16] Quinoidal porphyrins also have been synthesized.[17,18]) The valence-bond structure of Figure 2 is consistent with the observed bond lengths. The average difference in bond length between the formal single and double bonds for C$_\beta$−

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C_β is 0.053 Å, $C_\alpha-C_\beta$ is 0.055 Å, and $C_{meso}-C_\alpha$ is 0.070 Å. A comparison can be made with metalloporphyrin bond lengths obtained from the average of hundreds of crystal structures: $C_\beta-C_\beta$ 1.350 Å, $C_\alpha-C_\beta$ 1.441 Å, $C_{meso}-C_\alpha$ 1.393 Å, and $N-C_\alpha$ 1.378 Å.[19] The deviations from those bond lengths in Si(TPP)(THF)$_2$ can be understood by examining the molecular orbital into which the two extra electrons have been placed. A normal-valent porphyrin complex has two degenerate e_g LUMOs.[20] Addition of two electrons to one of the LUMOs causes a geometric distortion that lifts the degeneracy of the LUMOs. Inspection of a picture of the e_g LUMOs[21] makes clear that addition of two electrons to one LUMO would cause exactly the type of geometric distortion that occurs in Si(TPP)$_2$(THF)$_2$.

The geometry of a model compound, tetramethylporphyrinato(silicon)(OMe$_2$)$_2$ (Si(TMP)(OMe$_2$)$_2$), was optimized in a density-functional calculation (Gaussian 03,[22] B3LYP/6-31G*). It was slightly less ruffled than the crystal structure of Si(TPP)(THF)$_2$ (C_{meso} displacements of 0.884 Å), but the bond lengths were generally in very good agreement with those of Si(TPP)(THF)$_2$ (see Figure 2).

The aromaticity of porphyrins traditionally has been rationalized as a consequence of an 18 π-electron circuit that can be drawn in their valence-bond structure. The doubly reduced Si(TPP) should then be an antiaromatic 20 π-electron system, and in fact, one could view Si(TPP) as [20]annulene with eight carbons bound to a SiN$_4$ core (Figure 2). However, calculations of nucleus-independent chemical shifts (NICS)[19] and explicit calculation of the ring currents[23] indicate that, in metalloporphyrins, the whole ring system is involved in the aromaticity. We performed similar NICS calculations on the optimized structure of Si(TMP)(OMe$_2$)$_2$ at the centers of the two inequivalent pyrrole rings (points *a* and *c* in Figure 2) and the midpoint of two C−N bonds (point *b*). The NMR resonances of nuclei inside an antiaromatic ring are shifted downfield by the paratropic ring current,[24] and NICS values inside the ring are positive, the opposite effects as those inside an aromatic ring. A calculated NICS value of +39.0 at *b* indicates a strong paratropic ring current in Si(TMP)(OMe$_2$)$_2$. The value at *c* is +16.1 and at *a* is +10.2, and those lower values are likely due to a division of the macrocyclic ring current into the two paths available through the pyrrole rings. It should be noted that there is not universal agreement that a molecule that sustains a paratropic ring current should necessarily be defined as antiaromatic.[25]

Several pieces of NMR evidence indicate the presence of a strong paratropic ring current in Si(TPP)(L)$_2$, despite its ruffled structure. The ^{1}H NMR spectrum of Si(TPP)(THF)$_2$ is quite complicated, probably due to hindered rotation of the THF ligands and/or the phenyl groups, in conjunction with fluctuations of the ruffle of the molecule, so we will discuss NMR data from Si(TPP)(py)$_2$ instead. In the ^{1}H NMR spectrum of Si(TPP)(py)$_2$ in d_8-toluene, the (thermally averaged, see below) C_β protons are shifted far upfield to 1.29 ppm, as expected for nuclei outside an antiaromatic ring. (The dianion of tetratolylporphyrinato(zinc) has been generated in d_8-THF, and its C_β protons exhibited a similar upfield shift to −0.9 ppm.[26]) The 2-, 3-, and 4-protons of the coordinated pyridine are downfield at 20.35, 10.31, and 9.74 ppm, respectively, as expected for nuclei near the center of an antiaromatic ring. It was possible to observe the ^{29}Si NMR signal by a ^{1}H−^{29}Si HMBC experiment, where Si is coupled to the 3-H of the pyridine ligands. The ^{29}Si chemical shift of −93 ppm (calcd for Si(TMP)(OMe$_2$)$_2$: −89 ppm) can be compared to values of about −218 ppm in aromatic Si porphyrins;[27] the ^{29}Si resonance of antiaromatic Si(TPP)(py)$_2$ is shifted downfield by 125 ppm.

In the valence-bond structure of Figure 2, there are two chemically inequivalent types of C_β carbons (and hydrogens bound to them). Calculations indicate a 0.55 ppm ^{1}H NMR chemical shift difference and a 14.2 ppm ^{13}C NMR chemical shift difference between the inequivalent nuclei. However, the ^{1}H and ^{13}C NMR spectra of Si(TPP)(py)$_2$ in d_8-toluene between 22 and −40 °C display only one ^{1}H and one ^{13}C NMR resonance for these nuclei, indicating that interconversion of the single and double bonds is occurring rapidly (if the ruffle is static, this is an interconversion of enantiomers). Cyclobutadiene undergoes a similar interconversion rapidly even at 25 K.[28] In contrast, the crystal structure of Si(TPP)(THF)$_2$ clearly shows that at 100 K in the solid state the structure is static. It is likely that a combination of the lower temperature and the collective intermolecular interactions in the solid state makes it possible to observe the bond length alternation in the crystal structure.

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Supporting Information Available: Experimental details and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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